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Correlative study of optical, electrical and thermal transport properties of $Se_{100-x}In_x$ chalcogenide glasses

ABHAY KUMAR SINGH, KEDAR SINGH*

Department of Physics, Banaras Hindu University, Varansi-221005, India

The measurements of optical energy band gap, dc electrical conductivity and thermal conductivity of $Se_{100-X}In_x$ (X= 0, 5, 10, 15 and 20) chalcogenide glasses have been carried out at room temperature. The measured values of electrical conductivity and thermal conductivity are used to determine the Wiedemann-Franz ratio of the said materials in the composition range of variation. The variation of electrical and thermal conductivity have been found maximum at 10 at.wt.% of Indium (In). The variation of optical energy band gap and Wiedemann-Franz ratio have found minimum at 10 at. wt. % of In. The correlative results of optical energy band gap and dc electrical conductivity at various composition range of In can be consider as an experimental model for $Se_{100-x}In_x$ for chalcogenide glasses. These behaviors of materials could be understood on the basis of bond formation of Se and In at different compositions.

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1. Introduction

The glass-forming ability of chalcogens or pseudo chalcogens combinations have been known from several decades. This class of vitreous materials is just emerging from their infancy. The main attention paid to these materials relies on their large optical window extending in the mid-infrared and covering usually the two atmospheric windows lying from 3 to 5 and 8 to 12 μm. These low-phonon materials have to be considered as heavy anion glasses since sulfur (S), selenium (Se) and even tellurium (Te) are the main constituents of their compositions. This situation leads to fundamental vibrational modes shifted far in the IR and rending these glasses interesting for the fabrication of thermal-imaging systems [1].This exceptional transparency associated with suitable viscosity/temperature dependence creates a good opportunity for the development of molded optics for low-cost infrared cameras. There were also noticed that chalcogenide glasses exhibit some unique properties such as: photo-darkening [2], giant photo-expansion as well as photo-fluidity [3], Se-In glassy alloys are also used in photo cell.

The optical, electrical and thermal properties of chalcogenide glasses have studied extensively in recent years [4]. The glassy Se element is selected because of its wide commercial applications [5]. Due to unique IR transmission and electrical properties of Se makes it to useful for several applications, such as threshold switching, memory switching, inorganic photoreceptors, detection through lenses and optically wave guide e.g. in welding and surgery [6-8].

Besides of several discrete reports are on optical energy band gap, dc electrical conductivity and thermal conductivity of $Se_{100-x}In_x$ chalcogenide glasses. There have not been made any serious afford for their correlative work. In this research paper, we have reported the correlative work between optical energy band gap and dc electrical conductivity, and other correlation of thermal conductivity and dc electrical conductivity. Finally, we have calculated Wiedemann-Franz ratio of Se_{100-x} In_x (X= 0, 5, 10, 15 and 20) chalcogenide glasses at room temperature.

2. Material preparation and experimental techniques

In this research work, quenching method has been adopted to prepare $Se_{100-x}In_x$ (X= 0, 5, 10, 15 and 20) chalcogenide glasses. The desired amount of elements of high purity (99.999) were weighed the desired composition ratio of elements sealed into quartz ampoule (7 cm and internal diameter 8 mm) in a vacuum at 10^{-6} Torr and heated in a furnace, where temperature was raised at a rate 3-4^{0}C/min up to 900^{0}C and kept around the temperature for 9-10 hours, to ensure the homogeneity of the samples. The molten samples were then rapidly quenched into ice cooled water. Samples were obtained by quenching, in the form of glasses. The amorphous nature of samples has been confirmed through X-ray diffraction. These bulks glasses were crushed to fine powder. The pellets of thickness 1mm and diameter 12 mm were prepared by pressure machine at load of 5 tons. The reflection spectra of $Se_{100-x}In_x$ (X= 0, 5, 10, 15 and 20) had been taken by Hitachi model U-3400 spectrometer at room temperature and normal pressure. The dc electrical conductivity had been measured by Keithley high resistance meter/ electrometer 6517A. The thermal conductivity measurements had been done by transient plane source (TPS) techniques [9], which is advance technique for measurement of thermal conductivity.

3. Results and discussion

The measured result of optical energy band gap and dc electrical conductivity of $Se_{100-x}In_x$ (X= 0, 5, 10, 15 and 20) chalcogenide glasses are plotted in Fig.1.

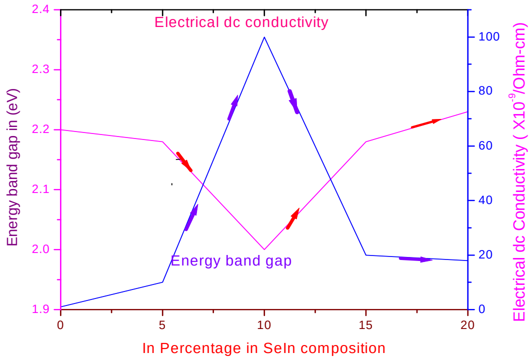

Fig. 1. Variation of energy band gap and dc electrical conductivity at different (In) concentration.

The optical energy band gap and dc electrical conductivity varies with In concentration. It is observed from Fig.1, at lower concentration of In (up to 5 at. wt.%) optical energy band gap is nearly constant. Further, addition of In content glassy system shows drastically decrease of the energy band gap and reaches minimum at 10 at. wt. of In . Further addition of In at. wt.% in $Se_{100-x}In_x$, the glassy system shows an increase in the optical energy band gap and finally it reaches a value upto 2.3 eV, then after its nearly become constant [10].

It is observed from Fig.1, the dc electrical conductivity vary with indium concentration. It follows same variation trend as optical energy band gap variation, but in reverse direction. The dc electrical conductivity increases rapidly with In concentration and found to maximum at 10 at wt% of In. Further, increase of In concentration in Se, the glassy system, shows drastically decrease in dc electrical conductivity up to 15 at. wt.% of In. Then after at higher concentration of In, glassy system shows dc electrical conductivity nearly becomes constant [11].

As shown in Fig.1, the more variation can occur in both optical energy band gap and dc electrical conductivity at 10 at. wt.% of In. From Fig.1, we are able to indicate the critical values of energy band gap and electrical conductivity of $Se_{100-x}In_x$ chalcogenide glasses at the concentration range 5-15 at. wt % of indium, with the help of single composite figure. The concentration range of In at which, $Se_{100-x}In_x$ chalcogenide glasses are showing technological importance. Under this composition range Se-In chalcogenide glasses probably applicable as: fast optical switching, signal regeneration and optical bio sensors [12]. The Fig.1 also provide us to some additional information about to predict the approximate (because we can not prevent experimental error) values of energy band gap and electrical conductivity only on choice of indium concentration range for $Se_{100-x}In_x$ chalcogenide glasses.

The experimental results of energy band gap are interpreted as, the type of bonds, which are expected to occur in $Se_{100-x}In_x$ chalcogenide glasses are Se-Se, Se-In and In-In with bond energies 79.5, 54.0 and 24.0 K cal/ mole respectively [13]. In the $Se_{100-x}In_x$ glassy system ≤ 5 atomic percentage of In concentration Se-Se homopolar bonds are in dominant conditions and ≥ 15 atomic percentage of In concentration In-In homopolar bonds are in dominant conditions. When Indium atomic percent 5 to 10 at. wt. % then Se-In glassy system are formed the Se-In heteropolar bonds and these hetropolar bonds are in dominant condition. Such type of bonding is formed due to presence of chemical disordering and defect in bulk materials [14].

The dc electrical conductivity can be influenced by the structural change in $Se_{100-x}In_x$ glassy system. It can be explained by band structure of Se-In, which have nine lowest lying bond filled by the eighteen valance electrons of the unit cell, even if the lower symmetry of monoclinic Se-In leads to much stronger orbital mixing. The lowest lying bands mainly have Se s character. The upper band has predominant In s character and correspond to the In-In covalent bond (molecular bonding σ orbital). The six bonds have predominant Se p character. The upper valance bond has predominant Se P_z character. These valance electron pairs responsible for inter interaction. The In character dominants in the lowest conduction band, although there is also a very sizeable contribution of the Se p orbitals (i.e anti bonding In-Se, σ orbitals) [15].Of course in view of above explanation, we can say that at 10 at. wt.% of In the glassy system posses the maximum chain length and heavily crosslink with In concentration, which is responsible for maximum electrical conductivity at 10 at. wt% of In as shown in Fig.1.

The variation of thermal conductivity and dc electrical conductivity with In concentration shown are in Fig.2.

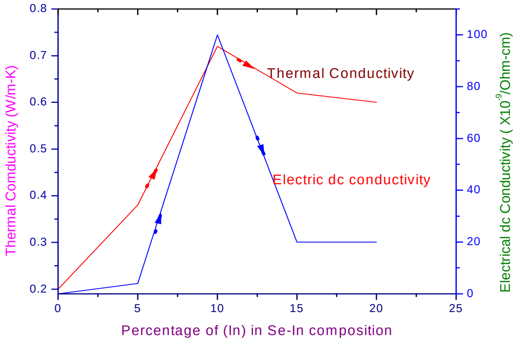

Fig. 2. Variation of thermal conductivity and dc electrical conductivity at different (In) concentration.

It is observed from Fig.2 that thermal conductivity and electrical conductivity increased with In concentration and both are maximum at 10 at. wt.% of In. But variations of both (thermal conductivity and electrical conductivity) are not same, even though both quantities are showing maxima at 10 at. wt. % of In. Beyond the 10 at wt.% of In both quantities decreases rapidly up to 15 at. wt.% of In, dc electrical conductivity decreases much rapidly to thermal conductivity, after 15 at. wt.% of In both quantities are nearly constant.

Since, below the 5 at. wt.% of In, Se-In glassy system are more chemically ordered i.e. less disordered glassy system and there energy band 2.2eV. Despite of well chemically ordered glassy system, it is quiet possible a few electron hole pair available for conduction at lower concentration of In. Further, increase of In concentration in Se-In, increases the disorderedness of the system, Due to this, dc electrical conductivity has been reached at maximum at. 10 at. wt. % of In. Further, more addition of In content, dc electrical conductivity decreases upto certain value and after that it nearly becomes constant, as we have discussed earlier in this study.

The total thermal conductivity has been calculated by the following expression for τ^{-1}reported recently in [16].

$$\tau^{-1} = \tau_b^{-1} + K_1\omega^4 + K_2 T\,\omega^3 \exp(-\Theta/bT) + K_3\,\omega^2$$

The first term on the right hand side $\tau_b^{-1} = v/d$ corresponds to the scatterings of phonons at the sample boundary (d- is the corresponding mean free path), the second terms ($K_1\omega^4$) to correspond to Rayleigh scattering at point defects, third one corresponds to ($K_2T\,\omega^3 \exp(-\Theta/bT)$) to phonon –phonon Umklapp process, and fourth term proportional to ω^2 at low temperature.

Since we have measured the thermal conductivities at room temperature, we can not completely ignore the fourth term, reported as Khadjai et. al [17].The contribution to the relaxation rate proportional to phonon scattering by crystal lattice distortion field produce by point defects in bulk chalcogenide. At room temperature the maximum possible mean free path($d=v\,\tau_b$) of phonon had to be restricted the minimum length l_{min}.The existence of smallest (l_{min}) possible room temperature conductivity defined by l_{min} was analyzed by Cahill et al [18] for the material with strong phonon scattering.

The $Se_{100-x}In_x$ glasses, at low concentration of In it make Se-Se bonds with bond length (232 pm), and more than 15 at. wt.% of In they can form In-In bonds with bond length (325 pm) respectively. The bond length of Se-Se is smaller than In-In bonds. The effective molecular weight of glasses decreases as the bond length increases, hence the density of localized state decreases [19]. Whenever In percentage 5-10 at.wt.%, Indium atoms heavily dissolved in Se chains. Therefore, the more addition of In breaks the Se chains into mixed rings to satisfy its coordination requirement [20] (i.e. at lower concentration of In, Selenium chains and rings are less effective while increase in In concentration increase the length of chains). Further, increase of In concentration in Se-In bring an increase in rings concentration and decrease in chain length which is probably responsible for the decrease of the thermal conductivity. Here we have explored the variation of electrical and thermal conductivities of $Se_{100-x}In_x$ systems in composite Fig.2 for better visualization and understanding of these two different phenonmena.

Finally, we have calculated Wiedemann-Franz ratio (L) for $Se_{100-x}In_x$ (X= 0, 5, 10, 15 and 20) chalcogenide glasses. Wiedemann-Franz law given as:

$L = K / \sigma T$

K- Thermal conductivity

σ – dc electrical conductivity

T- Temperature in (K)

The values of calculated ratio (Wiedemann-Franz) with In concentration plotted in Fig. 3.

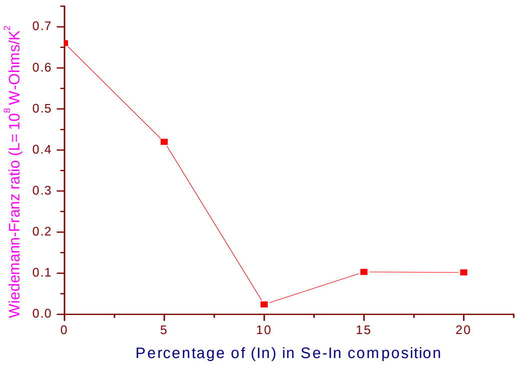

Fig. 3. Variation of Wiedemann-Franz ratio at different (In) concentration.

It is observed from Fig.3 that, a sharp decline in Wiedemann-Franz ratio values upto 10 at. wt.% of In. Then it increases upto 15 at. wt % of In and more than 15 at. wt % its nearly become constant.

It is also observed from Fig.3 that, maximum value of Wiedemann-Franz ratio at 0 at wt. % of In (i.e. Pure Se). It was reported in various text books that Wiedemann-Franz ratio values are constant for pure materials at different temperatures. Here we have taken constant room temperature and varied composition ratio of chalcogenide alloy. Due to this we have found different values of Wiedemann-Franz ratio.

4. Conclusion

A systematic study of the $Se_{100-x}In_x$ (X= 0, 5, 10, 15 and 20) chalcogenide glasses leads the following conclusions:

(i) The electrical conductivity and thermal conductivity are maximum, optical energy band gap and Wiedemann-Franz ratio is minimum of $Se_{90}In_{10}$ chalcogenide glass. Therefore, $Se_{90}In_{10}$ glass can be considered as critical composition of $Se_{100-X}In_X$ series.

(ii) Based on above study, it is found that for device fabrication the best composition is $Se_{90}In_{10}$ of $Se_{100-X}In_X$ series .

(iii) Fig.1 can use as an experimental model to locate the values of energy band gap and dc electrical conductivity at different concentration of Se-In chalcogenide system.

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*Corresponding author: kedar_abhay@rediffmail.com