ENERGY BAND GAP OF Se$_{100-X}$In$_X$ CHALCOGENIDE GLASSES

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The energy band gaps of Se$_{100-X}$In$_X$ (X = 0, 5, 10, 15 and 20) chalcogenide glasses have been studied at room temperature and normal pressure. The reflections spectra of these glasses are recorded by Spectrophotometer in the wave length region from 300 to 800 nm. From the analysis of the reflection spectra the optical energy band gap is determined. This is found to vary from 2.00 to 2.23 eV. The energy band gap is minimum in case of Se$_{90}$In$_{10}$ chalcogenide glass. This is suggestive of the fact that Se$_{90}$In$_{10}$ can be considered as a critical glass, which becomes chemically ordered for the said concentration of Indium. Such type of behaviour can be explained on the basis of the presence of high density of localized states in the band structure in Se$_{90}$In$_{10}$ chalcogenide glass.

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1. Introduction

Chalcogenide Semiconducting alloys have found application not only due to their electrical and thermal properties, but also due to their optical properties. Chalcogenide glasses have recently attracted a great deal of interest because of many applications as solid state devices both in scientific and technological field [1]. The current interest in chalcogenide materials centers on x-ray imaging and photonics [2]. Many amorphous semiconducting glasses, in particular selenium, exhibit [3] a unique property of reversible transformation. This property makes these glasses very useful in optical memory devices. However, the shortcoming of pure glassy selenium for its practical application includes its short lifetime, low sensitivity and thermal instability. To overcome these difficulties certain additive are used and specially the used to Se-Te, Se-Sb and Se-In binary alloys is of interest owing to their various properties like greater hardness, higher sensitivity, higher crystallisation temperature, higher conductivity and smaller ageing effect as compared to pure selenium [4] and several attempts have been made to utilize them in solar cells [5, 6]. Indium mono selenium has an energy band gap about 1.3 eV [7], this value is close to the theoretical optimum for solar energy conversion. Thus the system Se$_{100-x}$In$_x$ could have attractive characteristics for solar energy conversion especially in the form of amorphous or polycrystalline state.

To make the semiconducting glasses useful in the above mentioned application, it is very important to investigate their optical properties (like reflection spectra) these are important parameters for scientists and technocrats to decide its end use. In the present study the reflection spectra of Se$_{100-x}$In$_x$ (x =0, 5, 10, 15 and 20) chalcogenide glasses are recorded by a Hitachi spectrophotometer model-3400 in the wave length from 300 to 800 nm.

2. Material preparation

In the present research work quenching method has been adopted to prepare the glassy $Se_{100-x}In_x$ (X = 0, 5, 10, 15 and 20) chalcogenide glasses. The desired amounts of the elements of high purity (99.999) were weighed using an electronic balance. The highly pure material having the desired compositional ratio of elements were sealed into quartz ampoule (length 5 cm and internal diameter 8 mm) in a vacuum of 10^{-6} torr and heated in a furnace where temperature was raised at a rate of 3-4 ^{0}C/min up to 900 ^{0}C and kept around that temperature for 9-10 hours, to ensure the homogeneity of the samples. The molten samples were then rapidly quenched in ice cooled water. Sample obtained by quenching were in the form of glasses. The phase characterization has been confirmed through X-ray diffraction. These bulk glasses were then crushed to fine powders by mortal & pastel. The pellets of thickness 1 mm and diameter 12 mm were prepared by a pressure machine at a load of 5 tons. The reflection spectra of these material for different concentrations of In in Se-In system have been taken by spectrophotometer Hitachi modal U-3400 at room temperature and at normal pressure.

3. Characterization of sample

The optical reflectance measurement of $Se_{100-x}In_x$ (x = 0, 5, 10, 15 and 20) in bulk form have been taken at room temperature from 300 to 800 nm wave length range using a Hitachi U-3400 UV-VIS-NIR double spectrophotometer. The optical band gaps of these materials were determined with the help of reflection spectra. Almost all the samples have direct band gap. As per well known relation of Tauc [8], the absorption coefficient for direct band gap material is given by

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (1)$$

where $h\nu$ is the photon energy , E_g is the band gap and A is constant which is different for different transitions. The absorption coefficient α may be written in terms of reflectance as [9]

$$2\alpha t = \ln[(R_{max.} - R_{min.})/(R - R_{min.})] \qquad (2)$$

where t is the thickness of the sample and R is the reflectance for any intermediate photon energy. The reflectance falls from $R_{max.}$ to R_{min} due to the absorption of light by the material.

4. Results and discussion

The reflection spectra of these samples and for different compositions are shown in Fig.1 As is observed from Fig.1, the reflection decreases with decrease in wave length. Sudden fall present at a particular wave length, indicates the presence of the optical band gap in these samples.
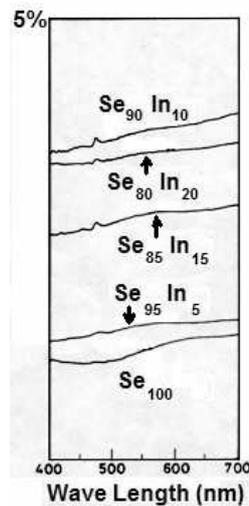

Fig. 1. Reflection spectra of $Se_{100-x}In_X$ (x = 0, 5, 10, 15 and 20).

A graph has been plotted between $(\alpha h\nu)^2$ or $h\nu[(R_{max}-R_{min})/(R-R_{min})]^2$ as ordinate and $h\nu$ as abscissa and a straight line is obtained . The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of band gap of these material. In Fig.2 we plot a graphs between the square of $h\nu$ $ln[(R_{max} - R_{min})/(R - R_{min})]$ and $h\nu$, for the determination of band gap. The band gap of $Se_{100-x}In_x$ (x = 0, 5, 10, 15, and 20) varies from 2.00 to 2.23 eV. The compositional dependence of the band gap is shown in Fig.3.

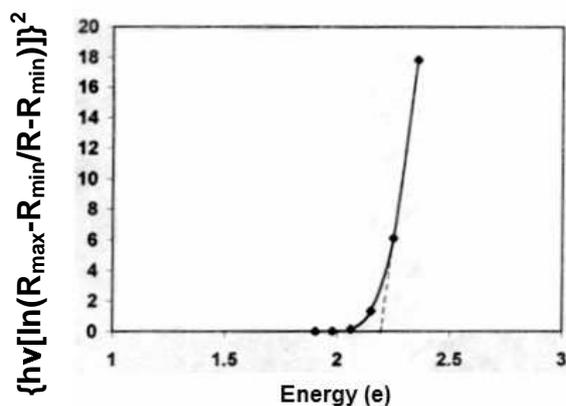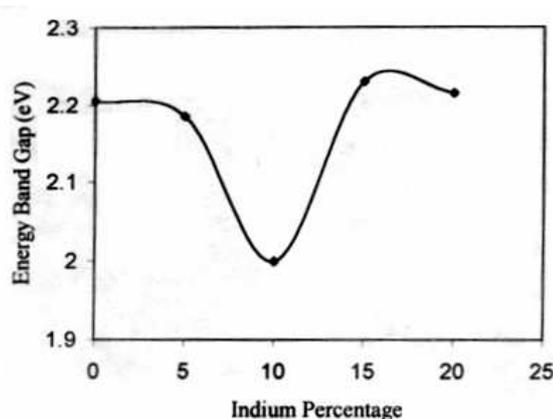Fig. 2. Energy band gap determination of Se_{100}.

Fig. 3. Variation of band gap with composition $Se_{100-X}In_X$ (x = 0, 5, 10, 15 and 20).

It can be observed from Fig.3 that energy band gap is minimum at 10 at % of indium in Se-In glasses. It has been indicated [10] that in selenium containing alloys, there is a tendency to form polymerization network glasses and the homopolar bond is qualitatively suppressed. Energy band gap decreases up to 10 at % of indium, and with further addition of indium in Se, the energy band gap becomes almost constant at higher atomic percentage of indium moreover, at lower percentage of indium, energy band gap slowly decreases. It is indicated that addition of indium in Se system, Se-In bond forms, carrier concentration increases, hence energy band gap of system decreases. Further addition of indium in Se system, In-In bond forms, volume of this system increases, molecular density of system decreases, thus decreasing carrier density of this system, hence increasing energy band gap. Such type behaviour of energy band gap with increasing indium impurity in $Se_{100-x}In_x$ glasses may be explained by considering the structural changes occurring due to the further addition of indium atoms. The generally accepted structural modal of amorphous Se includes [11] two molecular species, meandering chain, which contains helical chain of trigonal Se and Se_8 rings molecules of monoclinic Se.

As for as K- absorption edge study [12] of Se is concerned, it is found that behaviour of indium is similar to that of Sb and both make bond with Se. Therefore, as In atoms are incorporated they probably are dissolved in the Se chains and increasing relatively the number of Se_8 rings while the number of long Se-Se chain decreases.
It is reported [13] that glass transition temperature (T_g), crystallization temperature (T_c), the difference ($T_c - T_g$), glass transition activation energy and crystallization activation energy are minimum at 10 at % of indium in Se-In system. Effective thermal conductivity and effective thermal diffusivity found to maximum at 10 at % of indium in Se-In system. [14].

The experimental results of energy band gap is interpreted as follows, the type of bond expected to occur in $Se_{100-x}In_x$ system are Se-Se, Se-In, and In-In with bond energies 79.5, 54.0 and 24.0 K cal/mol, respectively [15]. Here Se-Se, In -In is homopolar and Se-Te bond are heteropolar .The average energy of homopolar bonds is nearly equal to the energy of heteropolar bonds. As strong Se-In bonds are energetically favoured compared to In-In bonds [16] , it is predicted that system exhibits a tendency for chemical ordering which tends to form microscopic molecular species. Addition of indium in Se system introduces In-In and In-Se bonds in Se_8 rings. It may be noted that bond length of In-In is larger than Se-Se bond. This may increase the volume of the system, hence the effective molecular weight decreases. Minimum energy band gap at 10 at. wt.% in $Se_{100-X}In_X$ system can be explained on the basis of the model of density states in amorphous solids proposed by Mott

and Davis [17]According to this model , it is assumed that the width of the localized states near the mobility edge depends on the degree of disorder and defects present in the amorphous structure. Davis and Mott [18] reported that the presence of high density of localized states in the band structure is responsible for lower energy band gap, hence density of localized state decrease so energy band gap increase.

5. Conclusion

Addition of indium in selenium has been found to vary the important optical/electronic parameter: the band gap. Tentative reasons for this variation have been put forward in terms of creation of Se-In bonds in Se_8 rings. In addition to this the disorder is also thought to be responsible for the decrease in density of localized states, hence resulting in lowering of band gap for specific composite $Se_{90}In_{10}$.

Acknowledgement

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