INVESTIGATION OF OPTICAL ABSORPTION IN $Te_5(In_xSe_{100-x})_{95}$ GLASSY ALLOYS

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An account of optical absorption measurements made on thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys ($10 \leq x \leq 25$) prepared by vacuum evaporation is presented. These measurements are made on the as-prepared and annealed samples. It is observed that annealing affects the optical properties and causes a reduction in the energy range of tail states and an increase in the optical energy gap in all the alloys. The mechanism of optical absorption follows the rule of non-direct transitions. The results obtained for different samples are compared with each other.

1. Introduction

Chalcogenide glasses have attracted lot of attention in the field of electronics as well as in optics due their peculiar properties suitable for processing of devices for electrical switching and memories, optical memory applications, x-ray imaging etc. These materials in particular selenium exhibit a unique property of reversible transformation [1], which makes these glasses useful as optical memory devices. The effect of alloying Te into a-Se [2,3] has been reported and it is found that the incorporation of Te results in dissociation of long polymeric chains and eight member rings of amorphous selenium [4]. This makes Se-Te alloys more important as compared to a- Se due to distinct advantages (greater hardness, better photosensitivity, lesser ageing effects etc.) and hence find applications as recording layer material in optical phase change technique [5,]. However, in these alloys limited reversibility [6] and low glass transition and crystallization temperatures are serious drawbacks. These drawbacks can be overcome by addition of third element as a chemical modifier as it is reported to expand the glass forming region and also creates compositional and configurational disorder [7]. The addition of dopant [In] can modify the lattice perfection and optical properties, which play a major role in device preparation. Thus the optical absorption properties of a-$Te_5(In_xSe_{100-x})_{95}$ alloys are interesting to study in detail from basic as well as application point of view.

The experimental details of sample preparation and optical absorption measurements are described in section 2. The results pertaining to as-prepared and annealed samples are presented and discussed in section 3. The last section contains the conclusions drawn from the present work.

2. Experimental

Different compositions of $Te_5(In_xSe_{100-x})_{95}$ glassy system (x = 10, 15, 20 and 25) were prepared in bulk form by melt quenching technique. Materials of 99.999% purity weighed according

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to their atomic percentage are sealed in evacuated quartz ampoules (~10^{-5} Torr). The sealed ampoules were heated to 1000° C in an electric furnace at the heating rate of 2-3°C /min.

The ampoules were frequently rocked for about 10 hours at the highest temperature to make the melt homogenous. The quenching is done in ice-cooled water. X-ray diffraction pattern of the samples were obtained, which confirmed the glassy nature of the material.

Bulk as obtained was used for preparation of planar thin film sample on a well-degassed corning glass slide by vacuum evaporation technique keeping the substrates at room temperature and base pressure of ~10^{-5} Torr. The thickness of thin film samples ranged from 0.2~0.5 μm. The optical absorption of thin films was measured using Hitachi U-3400 computerized spectrophotometer with double monochromator in the range 380-800nm. The results were obtained as α.t versus wavelength, where α is the absorption coefficient and t is the thickness of the film. These studies were made on both the as-deposited and annealed samples. The thin film samples were annealed in absence of light for one hour under vacuum (10^{-3} Torr) at a fixed temperature (340K).

3. Results and discussion

Planar thin film samples of different compositions of $Te_5(In_xSe_{100-x})_{95}$ glassy system have been used for optical absorption studies. In this study an effort is made to highlight both the optical features and the effect of annealing on different parameters of these alloys.

Fig. 1 shows the variation of α.t with energy in as-prepared thin films of different compositions, x = 10, 15 20 and 25 of the present glassy system. Similar behavior of absorption with energy is observed in annealed thin film samples of different alloys as shown in figure 2. From the data in Figs. 1 and 2, value of the absorption coefficient is obtained for both as-prepared and annealed films of each composition. The variation of α with energy is depicted in figure 3 for as-prepared samples of different compositions. Similar behavior is observed for annealed films though annealing causes a decrease in the absorption coefficient.
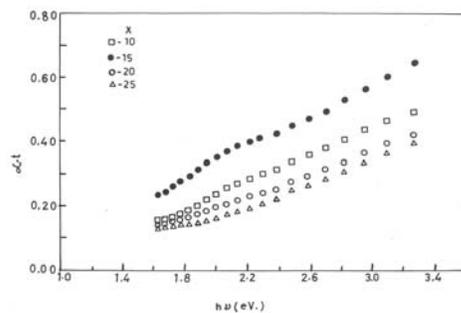

Fig.1 Variation of α.t as a function of photon energy in as-prepared thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys
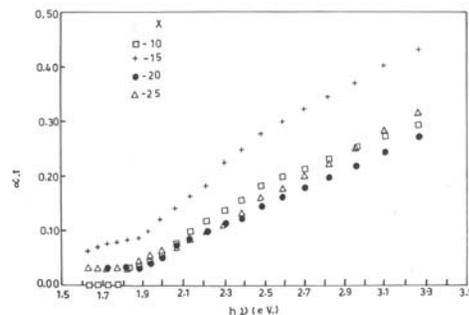
Fig.2 Variation of α.t as a function of photon energy in annealed thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys

In crystalline materials, electronic transitions between the valance and conduction bands start at the absorption edge corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valance band. In case when the extrema lie at the same point of k space, the transitions are called direct. Otherwise the transitions are possible only when phonon assisted and are labeled as non-direct [8]. However, as the crystalline to amorphous transition takes place, there is a shift of the absorption edge. The identification of optical absorption and other related processes occurring at energies below the energy gap E_g, with the presence of intrinsic, disorder induced localized states are least understood.
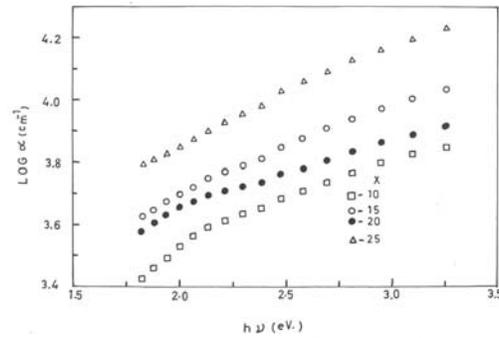
Fig. 3. Variation of the absorption coefficient (Logα) with energy in as-prepared thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys

In chalcogenide glasses, a typical absorption edge can be broadly ascribed to any of the three processes: (I) residual below gap absorption; (ii) Urbach tails and (iii) inter band absorption. Chalcogenide glasses have highly reproducible optical absorption edges, which are relatively insensitive to preparation conditions. Under equilibrium conditions, only observable absorption [8] with in the band gap accounts for process (i). In the second mechanism, the absorption edge depends exponentially on energy; the absorption coefficient $\alpha < 10^2$ cm^{-1} and increases exponentially with photon energy according to the so called Urbach relation [9] in ionic solids. In the high absorption region ($\alpha \sim 10^4$ cm^{-1}) it obeys the rule of non-direct transitions and the optical transitions between the valance and the conduction band are given by the relation [8]

$$\alpha = B(h\upsilon - E_g)^2 / (h\upsilon) \qquad (1)$$

where $h\upsilon$ is the incident photon energy, E_g, the optical energy gap, and B, the constant related to the extent of band tailing (δE) given as [10]

$$B = 4\pi\sigma_{min}/(nc\delta E) \qquad (2)$$

where, σ_{min} is the extrapolated d. c. conductivity as T approaches infinity, n is the refractive index and c, the velocity of light. A plot of $(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ known as Tauc's plot will be a straight line in such type of absorption. The intercept of the plot gives the value of the optical gap, and the slope gives the value of the constant B. This behavior is reported in number of chalcogenide glasses [11-13].
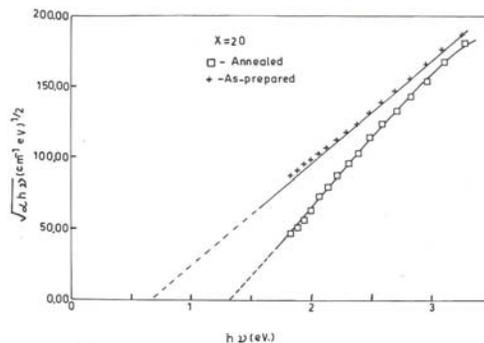

Fig. 4. Variation of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$. in as-prepared thin films of $Te_5(In_{15}Se_{85})_{95}$ glassy alloys; the solid lines represent the least square fit.

From the plots in Fig. 4 for x = 15 alloy, the absorption seems to be as result of non-direct absorption and the extrapolation of the linear portion of the curve is used to obtain the optical energy gap. Results for other compositions are found to be of similar nature. Values of the absorption

coefficient at a fixed energy for all compositions are listed in Table 1, and the values indicate that the absorption is caused by non-direct transitions. The values of optical gap (E_g) and constant B in both forms of each composition are determined from Tauc's plots and are presented in Table 1.

Table 1. Various parameters related to the optical absorption measurements for different compositions of $Te_5(In_xSe_{100-x})_{95}$ glassy system.

In% (x)	as-deposited			annealed		
	α (cm^{-1})	E_g (eV)	B^{-1} (cm eV)	α (cm^{-1})	E_g (eV)	B^{-1} (cm eV)
10	3.39×10^3	0.82	1.58×10^{-2}	1.10×10^3	1.50	1.09×10^{-2}
15	4.54×10^3	0.61	1.61×10^{-2}	1.80×10^3	1.35	1.15×10^{-2}
20	5.02×10^3	0.65	1.39×10^{-2}	2.03×10^3	1.31	1.04×10^{-2}
25	7.13×10^3	0.91	0.75×10^{-2}	3.16×10^3	1.42	7.89×10^{-2}

The values of E_g for a particular glass in the table suggest that annealing causes an increase in the optical gap. Such a behavior is perhaps due to a reduction in the disorder of the atomic bonding between neighbors leading to shrinkage of the band tailing adjacent to the band edge. This behavior is further supported by the change in B^{-1} values due to annealing. As seen from Table 1, B^{-1} decreases due to annealing in all compositions of the present system, which is in conformity with equation (2). Tauc's plots for as-prepared and annealed films of different compositions are shown in Figs. 5 and 6 respectively, which clearly show the similar nature of absorption in different alloys.
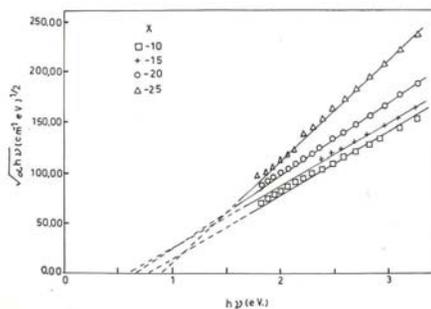

Fig. 5 Variation of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$. in as-prepared thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys; the solid lines represent the least square fit.
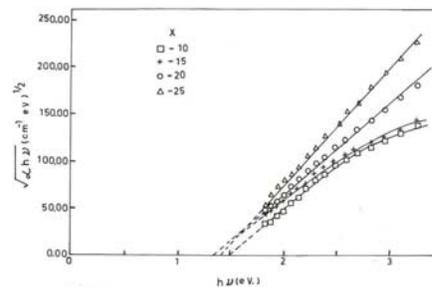

Fig. 6 Variation of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$. in annealed thin films of $Te_5(In_xSe_{100-x})_{95}$ glassy alloys; the solid lines represent the least square fit.

In present alloys, the energy gap is found to decrease with increasing In content and shows a minimum for x = 20. In alloys containing selenium, there is a tendency to form polymerization network glasses and the homopolar bond is qualitatively suppressed [14]. Energy band gap is reported to decrease due to addition of indium upto 10 % in Se. It is indicated that addition of indium in Se system, Se-In bonds form, carrier concentration increases, hence energy band gap of the system decreases. Further addition of indium in Se system, In-In bond formation takes place. Volume of this system decreases, molecular density increases, thus decreasing carrier density of this system, hence increasing energy band gap. Such type of behavior of energy gap with increasing indium content in Se-In glasses may be explained by considering the structural changes due to increasing indium concentration. Different bonds expected to occur in Se-In system are Se-Se, In-In and Se-In with bond energies 79.5, 24.0 and 54.0 K cal/mol respectively (15). The Se-Se, In-In are homopolar and Se-In are heteropolar. The average energy of homopolar bonds is almost equal to the energy of heteropolar

bonds. As strong Se-In bonds are energetically favored compared to In-In bonds [16], it is predicted that the 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 the bond length of In-In is larger than Se-Se bond, which may increase the volume of the system, hence effective molecular weight decreases. In $In_{20}Se_{80}$ alloy, [17] addition of Te at the cost of Indium increases the glass transition temperature due to decreasing Se_8 ring concentration and formation of Se-Te polymeric chains.

Se and Te being the elements of same group of the periodic table, most of the tellurium atoms are probably mixed in Se chains but, some of the tellurium atoms may not be incorporated in the chains. The Te atoms not incorporated into chains would act as ionized impurities forming positively charged localized states, since the electron affinity of Te (1.97 eV) is less than that of Se (2.02 eV). Similarly, the addition of In will induce more and more positively charged localized states, as the electron affinity of In is much lower than that of Se and Te. Therefore, an increase in defect states with increasing In concentration may be understood in terms of very low electron affinity of In (0.30 eV) as compared to Se or Te. In present glasses, the variation of E_g with In% seems to be explained in terms of the formation of Se-In bonds upto x=20. Further addition of indium seems to form In-In bonds, decreasing the volume of this system, hence increasing energy band gap.

The addition of indium in Se-Te causes an increase in the density of defect states which may be understood in terms of the values of electron affinity of In [18]. In present glasses the results may be explained on the basis of the model of density states in amorphous solids proposed by Mott and Davis [19]. 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 the defects present in the amorphous structure. Davis and Mott 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 states decrease so that the energy band gap increase.

4. Conclusions

Various parameters related to optical absorption have been obtained for $Te_5(In_xSe_{100-x})_{95}$ glasses. The absorption seems to be indirect in both as-prepared and annealed films of each composition. It is observed that annealing has a significant effect on the optical band gap and is in good agreement with the theory. The optical band gap is found to decrease up to x = 20 and thereafter it increases. This behavior has been explained due to increasing In content and average bond energy of the system.

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