

FTIR and Optical Properties of various Se-S-Zn Chalcogenide Glasses

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Abstract. Se-S-Zn chalcogenide glasses are prepared by melt-quenching technique. The amorphous nature of the glasses is ascertained by XRD patterns. In this work, the structural changes in these glasses are investigated by FTIR- spectra. An absorption band at 500cm^{-1} found in each glass is assigned due to the presence of Se_8 ring. The optical band gap is observed to decrease with increase in Zn content. This decrease has been explained on the basis of metallic bonding due to incorporation of Zn. The Urbach's energy is used to characterize the degree of disorder in amorphous solids. SEM has been used to prove the formation of nanosized particles.

1. Introduction

Recently, a great deal of work has been reported in the field of chalcogenide glasses due to their wide range of applications both in scientific and technological fields [1] such as in solid state devices, infrared optical fibres. These glasses exhibit unique IR transmission and electrical properties that make them useful for several applications such as threshold switching, memory switching, inorganic photoreceptors, detection through lenses and optical waveguide [2]. Amorphous Se is found to be useful as photo receptor in Xerox-graphy [2]. In case of Selenium (Se), each atom needs two neighbours to satisfy the valence requirements. This can be achieved either by the formation of small molecules (Se_8) or linear polymeric chain (Se_n) [3]. The properties of amorphous Se (a-Se) and the effect of alloying S into a-Se have been studied by various workers [3]. These studies indicate that when S is incorporated to amorphous Se, it is dissolved in the Se chains to satisfy its coordination requirements and to form a cross-linked structure which retards the crystallization probability. The addition of third element in Se-S glass converts it into an interesting material and new promising properties of the material are expected [4]. The addition of Zinc (Zn) to Se-S is expected to create the compositional and configurational disorder in the material. Optical properties of multicomponent chalcogenide glasses have attracted great attention because of their high transmittance in IR spectral region [5]. In our research paper, the optical properties of various compositions of Se-S-Zn chalcogenide glasses in terms of optical band gap and Urbach's energy are reported. The FTIR spectra of present glasses are also discussed.

2. Experimental details

Chalcogenide glasses $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 0, 2, 4$) are prepared by the melt-quenching technique. High purity (99.999%) constituent elements in appropriate proportions are weighed using electronic balance



and put into a quartz ampoule (length ~12cm, inner diameter ~14mm and outer diameter ~16mm). The ampoule containing chemicals (10g) is sealed in a vacuum of 10^{-3} Torr by using rotary pump and heated in a furnace where the temperature is raised at a rate of 4°C per minute up to 600°C and thereafter temperature is raised at a slower rate of 1.5°C per minute up to the temperature in the range $875\text{--}925^{\circ}\text{C}$ depending upon the composition of the sample. The ampoule is kept at this temperature for 15 hours. The ampoule is agitated frequently in order to intermix the constituents to ensure homogenization of the melt. The molten sample in quartz ampoule is rapidly quenched in ice-cooled water to get the glassy state. The amorphous nature of the samples is ascertained by XRD patterns as recorded by using Rigaku X-ray diffractometer. The SEM model JSM-Joel 6510 is used to study the microstructure of the glasses. The IR transmission spectra of these glasses in KBr pellets are recorded using Perkin Elmer Spectrophotometer in the wave number range $400\text{--}4000\text{cm}^{-1}$. The optical transmission spectra of all the samples are recorded using UV/VIS/NIR Spectrophotometer (Cary 5000) in the wavelength range $200\text{--}800\text{nm}$.

3. Results and discussion

3.1. X-ray diffraction and SEM studies

XRD patterns of various glasses are found to be similar and typical XRD patterns for sample with $x = 2$ and 4 are shown in Fig.1. Perusal of this figure shows that the samples exhibit the glassy (amorphous) behaviour with a broad hump. No peak corresponding to Zn is observed which indicates that Zn has completely entered the glass matrix. The microstructure of the glasses is identified by scanning electron microscopy (SEM) studies. The Fig.2 shows the typical SEM micrograph of studied glasses for $x = 2$ (at%) of Zn which is found to be a glassy (amorphous) nature of the sample.

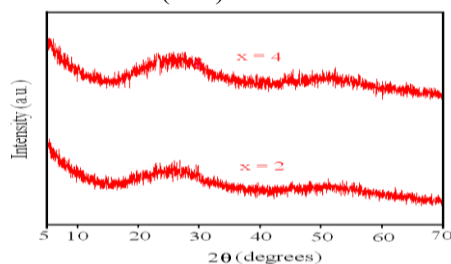


Fig.1 X-ray diffraction patterns of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ chalcogenide glasses: for $x = 2, 4$ (at %).

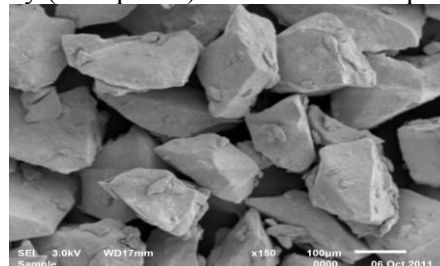


Fig.2 Typical SEM of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ chalcogenide glasses: for $x = 2$ (at %).

3.2. Fourier Transform Infrared (FTIR) Spectra

FTIR transmission study provides valuable information about the atomic configuration of glasses. The spectra of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 0, 2, 4$) chalcogenide glasses are shown in Fig.3(a-c). FTIR spectra of samples with $x = 2$ and 4 exhibit (except $\text{Se}_{72}\text{S}_{28}$) four absorption bands:

- i) band at about 3500 cm^{-1} ii) band at about 1500 cm^{-1} iii) band at about 1000 cm^{-1}
- iv) band at about 500 cm^{-1}

The intensity of all these bands is observed to increase with increase in Zn concentration (from $x = 2$ to $x = 4$). This may be due to the occurs of hetero-polar bonds like Zn-S, Zn-Se or Zn-S-Se. FTIR spectra of $\text{Se}_{72}\text{S}_{28}$ and $\text{Se}_{68}\text{S}_{28}\text{Zn}_4$ show some additional absorption peaks in region between $2500\text{--}3000\text{cm}^{-1}$ and $1500\text{--}2000\text{cm}^{-1}$ in mid-IR region. These absorption peaks may arise due to presence of H_2O and other impurity contents in glassy samples [6]. However, no such types of absorption peaks are observed in remaining glass sample. An absorption band observed at around 500cm^{-1} is assigned to the presence of Se_8 ring [7]. This absorption band is absent in $\text{Se}_{72}\text{S}_{28}$ glass. Another absorption band appearing at about 1500cm^{-1} is assigned to the presence of Zn-Se-Zn. Similar results have been reported by Goyal and Maan [8]. The absorption band at about 1000cm^{-1} is assigned to vibrational mode associated with mixed vibrations due to hetero –polar bonds like Zn-Se, Zn-S and/or Zn-Se-S [9]. From the energy point of view, the hetero-polar bonds are preferred compared to homo-polar bonds. Due to chemical ordering, the features such as the change in slope or kink occur for the various

properties and therefore, the glass structure is made of cross-linked structural units consisting of hetero-polar bonds only. Each constituent is coordinated by 8-n atoms, where n is the number of electrons in the outer shell (valence shell) and result in neglecting the other types of the bonds like dangling bonds and the other valence defects [10]. As the amount of Zn goes on increasing formation of hetero-polar Se-Zn bonds starts increasing at the expense of homo-polar bonds like Se-Se, S-S and Zn-Zn bonds [11]. So formation of Se-Zn and/or S-Zn bonds reduces the average energy of the system which consequently supports the decrease in optical band gap [12].

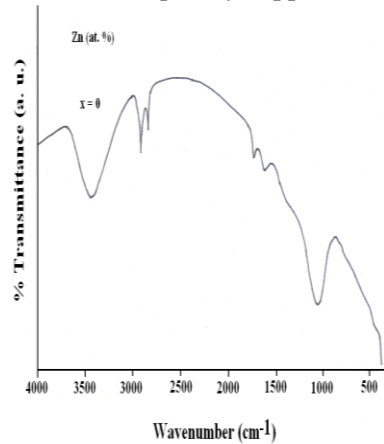


Fig.3 (a) FTIR spectrum of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 0$) glasses.

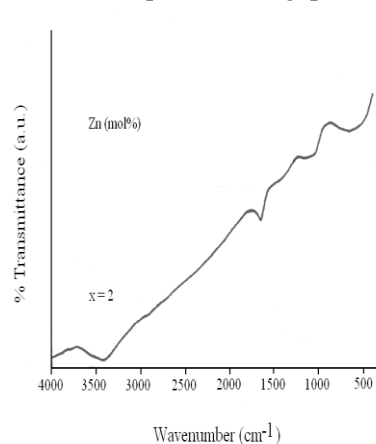


Fig.3 (b) FTIR spectrum of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 2$) glasses.

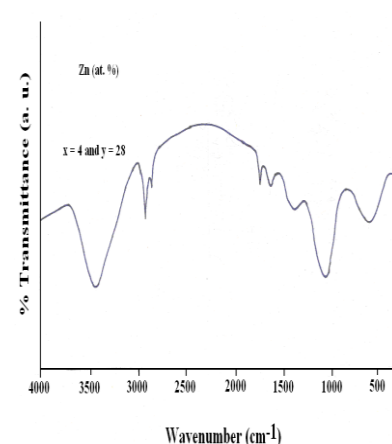


Fig.3 (c) FTIR spectrum of $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 4$) glasses.

3.3. UV-Vis absorption spectra

The band gap of glassy systems is obtained with the help of evaluated values of absorption coefficient (α) by using Tauc's relation [13].

$$\alpha h\nu = B(h\nu - E_g)^r \quad (1)$$

where B is the slope of Tauc edge called band tailing parameter that depends on the width of localized states [14] in the band gap (i.e. transition probability). E_g is the optical band gap of the investigated glasses and r is a number which characterizes the transition process. Plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) ($r = 2$) for $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ ($x = 0, 2, 4$) glasses are shown in Fig.4. Value of E_g is determined by extrapolation of the linear part of the plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) and it intercepts with the abscissa used value of E_g (at $\alpha = 0$, $E_g = h\nu$). The values of optical energy band gap (E_g) lie between 1.98- 2.81eV and it shows that the optical energy band gap is decreasing with increase in Zn doping. It can be suggested, following Kitao et al. [15], that the compositional change in the host material could exist by itself. This effect is due to the change in bond angles and/or bond lengths. Present results are consistent with the previous work dealing with the decrease of the energy gap with composition [16]. The decrease in optical band gap may be correlated with the electronegativity difference of the elements involved. According to Kastner et al. [17], the valence band in chalcogenide glasses is constituted by lone pair p-orbital contributed by the chalcogen atoms. These lone pair electrons will have higher values of energy adjacent to electropositive atoms than those of electronegative atoms [16]. Therefore, the addition of electropositive elements to the alloy may raise the energy of lone pair states which is further responsible for the broadening of valence band inside the forbidden gap. The electrogetivites of Se, S and Zn are 2.55, 2.58 and 1.65, respectively. From these electrogetivity values, it is clear that Zn is less electronegative than Se and S, so the substitution of Zn for Se and/or S may raise the energy of some lone pair states and hence broaden the valence band. This leads to band tailing and hence shrinking of the band gap thereby E_g value decreases with Zn content [16]. Further, the value of Urbach's energy ' ΔE ' has been calculated from the reciprocal of the slopes of the linear portion of curves between $\ln\{\alpha(\nu)\}$ and $h\nu$ i.e. Urbach's plots. In general, the materials with larger Urbach's energy would have greater tendency to convert weak bonds into defects. The

value of ' ΔE ' for the present glass system lies in the range 2.30- 3.21 eV which is increasing with Zn content, suggesting the glassy nature of our system.

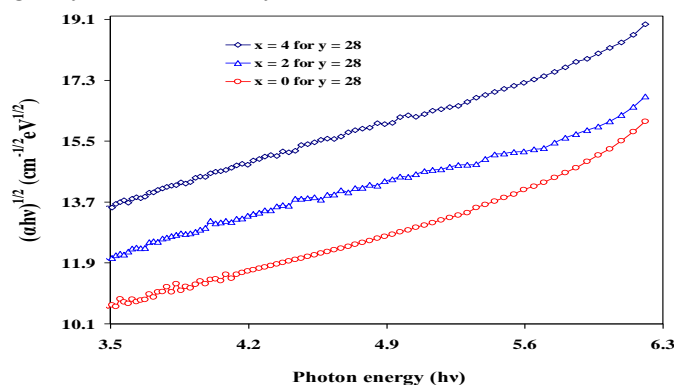


Fig.4 Tauc's plots for various $\text{Se}_{(72-x)}\text{S}_{28}\text{Zn}_x$ glassy alloys.

4. Conclusions

From XRD patterns, it is confirmed that the given samples are amorphous in nature. FTIR spectra suggests the formation/existence of the heteropolar bonds like Se-Zn, Se-S at the expense of homopolar bonds like Se-Se, Zn-Zn, S-S with increase in Zn content. The optical absorption in the given glass systems seems to be of indirect type and the optical band gap is found to decrease from 2.81 to 1.98 eV with the addition of Zn content. Urbach's energy increases confirming thereby the amorphous nature of the studied glasses.

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