Effect of CNT doping on optical properties of $Cu_5Se_{75}Ge_{10}In_{10}$ glassy alloys**

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Chalcogenide glasses of bulk Cu-Se-Ge-In with 1 wt% CNT were synthesized by melt-quench technique. Thin films of as-prepared and with 1 wt% CNT added Cu-Se-Ge-In glassy alloys were made by a thermal evaporation method. Optical properties were determined using a UV-vis spectrophotometer. The absorption (extinction) coefficient decreased with addition of CNT while the optical bandgap increased from 1.9 to 2.1 eV. The greater optical bandgap found in CNT-doped Cu-Se-Ge-In is explained on the basis of the Mott–Davis model of density of defect states.

Keywords: carbon nanotube, chalcogenides, extinction coefficient, photon energy

1. Introduction

Chalcogenide glasses (CHG) are traditionally composed of the divalent elements S, Se and Te combined with Ge, As, Sb, Si, P or other neighbouring atoms in the periodic table. Two characteristics of the constituent elements of these glasses should be emphasized. First, because of their large atomic masses they generate low phonon energies within the amorphous network and they confer wide optical transparency to the glass, extending far into the infrared. This property is a defining characteristic of chalcogenide glasses and has been the source of much research for infrared optics applications [1]. Second, the elements in these component have electronegativity close to 2 and therefore form well-defined directional covalent bonds following the $8-N$ octet rule; the structure of glass can be conveniently described as a network

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of covalent bonds, which lends itself well to modeling and simulations. These glasses typically possess a broad region of infrared transparency, limited visible transparency, low optical attenuation, high refractive index and high optical nonlinearity, and are generally stable with respect to atmospheric moisture [2].

CHGs have gained a lot of attention from researchers around the globe because they are among the most versatile functional candidates for active applications in photonics. CHGs are novel functional materials exhibiting striking electrical and optical properties [3]. CHGs are more flexible in their glassy states; their properties can be modified by doping with other additives or external influences like radiation, heat, pressure etc.

Binary and ternary chalcogenides have some drawbacks, such as low crystallization temperature, thermal stability and aging effects [4]. To overcome these issues quaternary or multicomponent alloys are being studied nowadays [5].

Investigation of the optical properties of chalcogenide–multiwalled carbon nanotube (CNT) composites could be interesting as these materials have been little investigated. CNT are allotropes of carbon with a hollow cylindrical structure. In recent years, CNT-doped materials have drawn the attention of researchers because of the unusual properties conferred by the CNT, with their high electrical conductivity, large surface area and low density; these novel composites are relevant candidates for applications in fields like microelectronics, electricity generation and storage and biotechnology [6]. CNT can effectively alter the electrical, mechanical, thermal, electrochemical and optical properties of composite materials at surprisingly low levels of doping [7]. The present paper focuses on the optical properties of multicomponent chalcogenides (Cu-Se-Ge-In) doped with multiwalled CNT for photonics applications.

2. Experimental

Bulk samples of $Cu_5Se_{75}Ge_{10}In_{10}$–CNT glassy alloys were prepared using a standard melt-quenching technique. Specific proportions of high purity (99.999%) Cu, Se, Ge and In according to their atomic weight percentages were sealed in a quartz ampoule (melting point 1650 °C) in a vacuum of 10^{-6} Pa. After sealing, the ampoule was kept in a furnace at a temperature of 1073 K for 10 h. The ampoule was constantly rotated to maintain the homogeneity of samples. Afterwards, the ampoule was melt-quenched in ice-cold water to solidify the contents. For preparation of glassy alloy doped with CNT, a small quantity of the sample of $Cu_5Se_{75}Ge_{10}In_{10}$ was crushed to a fine powder, mixed with 1 wt% multiwalled CNT (Sigma–Aldrich), sealed in quartz ampoules in a vacuum of 10^{-6} Pa and heated in a furnace at 900 °C for 12 h. Then the ampoule was melt-quenched in ice-cold water to obtain the final product.

The bulk samples were deposited on glass substrates to form thin films using the vacuum evaporation technique at room temperature and a base pressure of ~10^{-5} Pa. Samples were kept in a molybdenum boat inside the vacuum chamber. When the desired vacuum was reached, the samples were evaporated with a definite rate of deposition, measuring the thickness using a quartz crystal monitor. The prepared films were kept in the vacuum for 24 h. Normal incidence spectra of prepared thin films were obtained with the help of a double-beam UV-vis UV5704SS spectrophotometer (Electronics Corporation of India Ltd) in the wavelength range 300–900 nm.

3. Results and discussion

Fig. 1 shows the variation of transmittance T with wavelength λ in as-prepared Cu-Se-Ge-In and Cu-Se-Ge-In with 1 wt% CNT thin films. The curve shows various fringes due to interference. These fringes can be used to determine various optical constants, viz., extinction coefficient k, absorption coefficient α and optical bandgap E_g of prepared thin films.

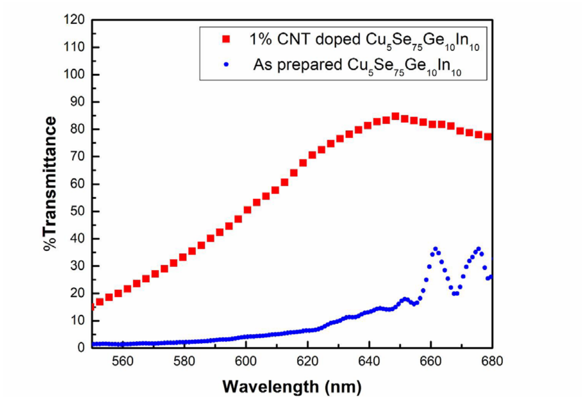

Figure 1. Variation of the transmittance (T) versus wavelength (λ) for as-prepared $Cu_5Se_{75}Ge_{10}In_{10}$ and 1 wt% CNT–$Cu_5Se_{75}Ge_{10}In_{10}$ thin films.

Fig. 2 shows the spectral dependence of k for the pure and CNT-doped thin films. The extinction coefficient of a material is a measure of the rate of decrease of transmitted light by absorption and scattering; its value was determined according to [8,9]:

$$k = \alpha \lambda / (4 \pi). \quad (1)$$

Similar trends of k with λ have been reported for other compounds [10]. It was observed that k decreases with CNT doping.

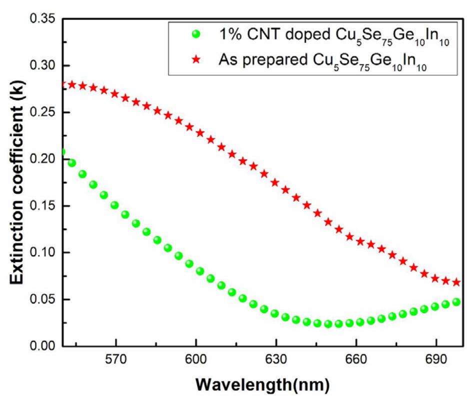

Figure 2. Variation of the extinction coefficient (k) versus wavelength (λ) for as-prepared $Cu_5Se_{75}Ge_{10}In_{10}$ and 1 wt% CNT–$Cu_5Se_{75}Ge_{10}In_{10}$ thin films.

The dependence of α on photon energy $h\nu$ for the thin films is presented in Fig. 3; α was determined by [11]:

$$\alpha = 2.303\, A / t \tag{2}$$

where A is the absorbance of the film and t its thickness. In pure $Cu_5Se_{75}Ge_{10}In_{10}$, the absorption coefficient increases with increasing photon energy, due to the presence of localized levels within the energy gap, which shifts the absorption edge to lower energies. After incorporation of CNT, α decreases, in concordance with an earlier result [12].

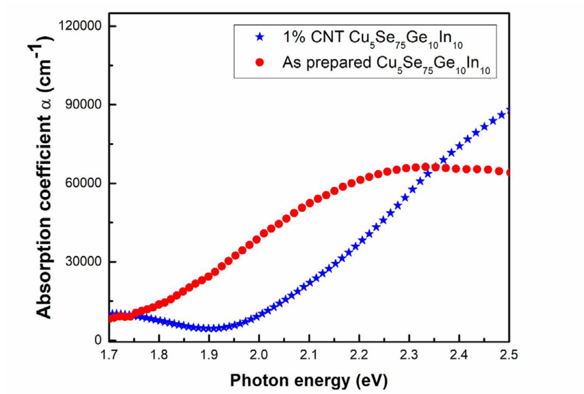

Figure 3. Variation of the absorption coefficient (α) versus photon energy ($h\nu$) for as-prepared $Cu_5Se_{75}Ge_{10}In_{10}$ and 1 wt% CNT–$Cu_5Se_{75}Ge_{10}In_{10}$ thin films.

The optical bandgap E_g can be determined from Tauc's relation [9]

$$(\alpha h\nu)^{1/m} = W(h\nu - E_g) \tag{3}$$

where W is the edge width parameter and m is an index of the nature of the electronic transitions by which absorption takes place. For an allowed direct transition $m = 1/2$, for an allowed indirect transition $m = 2$, for a forbidden direct transition $m = 3/2$, and for a forbidden indirect transition $m = 3$. We found that eqn (3) best fits our data when $m = 1/2$; i.e., absorption in both pure and 1 wt% CNT-doped $Cu_5Se_{75}Ge_{10}In_{10}$ thin films is via an allowed direct transition [13]. Hence $(\alpha h\nu)^{1/2}$ was plotted versus photon energy ($h\nu$) as shown in Fig. 4. The extrapolated intercept on the x-axis gives the value of E_g. It was observed that it increases with CNT doping. This increase may be interpreted according to the Mott and Davis model [14], which suggests that a decrease in the amount of disorder in a material or a decrease in the density of defect states (which may result from a decrease in the amount of disorder) increases the bandgap. Our results are in good agreement with earlier-reported results of other workers [15].

The values of the optical constants are collected in Table 1.

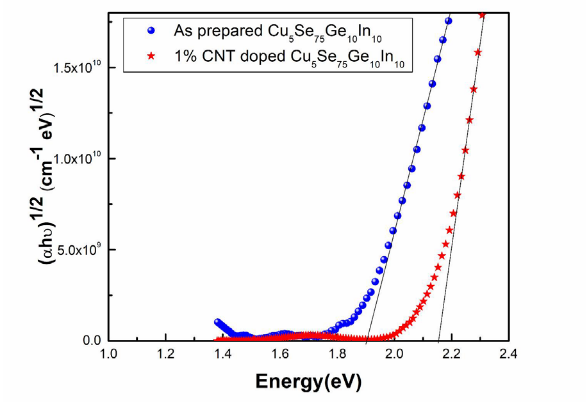

Figure 4. Variation of $[\alpha h\nu]^{1/2}$ versus photon energy ($h\nu$) for as-prepared $Cu_5Se_{75}Ge_{10}In_{10}$ and 1 wt% CNT–$Cu_5Se_{75}Ge_{10}In_{10}$ thin films.

Table 1. Optical constants of $Cu_5Se_{75}Ge_{10}In_{10}$ and $Cu_5Se_{75}Ge_{10}In_{10}$–1 wt% CNT

Specimen	k at 600 nm	α/cm^{-1} at 600 nm	E_g/eV
$Cu_5Se_{75}Ge_{10}In_{10}$	23.02×10^{-2}	4.85×10^4	1.90
$Cu_5Se_{75}Ge_{10}In_{10}$–1 wt% CNT	8.30×10^{-2}	2.30×10^4	2.15

4. Conclusions

The transmittance spectra of pure $Cu_5Se_{75}Ge_{10}In_{10}$ and 1 wt% CNT–$Cu_5Se_{75}Ge_{10}In_{10}$ thin films prepared by a thermal evaporation method have been measured and used to calculate various optical parameters. The optical bandgap increases with incorporation of CNT because of a decrease in defect states. The large absorption coefficient and compositional dependence of these materials make them promising for optical memory devices. Furthermore, the studied materials have bandgaps appropriate for solar cell applications.

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