

## Some physical properties of $\text{Se}_{0.8}\text{Te}_{0.2}$ amorphous chalcogenide system

A. F. MAGED<sup>\*+</sup>, G. A. M. AMIN<sup>\*</sup>, M. SEMARY<sup>\*\*</sup> and E. BORHAM<sup>\*</sup>

<sup>\*</sup> National Center for Radiation Reserch and Technology, (EAEA),  
P.O. Cod 11787 -Nasr City, Cairo , Egypt.

<sup>\*\*</sup> Faculty of science, Physics Dept., Cairo University

Corresponding author: Email: [migoali@yahoo.com](mailto:migoali@yahoo.com) or [magedali2000@eaea.org.eg](mailto:magedali2000@eaea.org.eg)

### Abstract

Glasses based on selenium and tellurium were carefully characterized to establish the interdependence between chemical composition and the magnitudes of the physical parameters. Optical measurements were performed on thin amorphous chalcogenide films from the system of pure ( $\text{Se}_{0.8}\text{Te}_{0.2}$ ) and metal doped ( $\text{Se}_{0.8}\text{Te}_{0.2}$ )<sub>0.9</sub>M<sub>0.1</sub> (M= Cu, Ag and Sn). Parameters considered in this paper are density, molar volume, the concentrations of metal atoms per unit volume, and optical energy gap. Bulk  $\text{Se}_8\text{Te}_2$  alloy was prepared by the standard melt quenching technique and the different metals were added to the binary system using the same technique. Thin films of the prepared compositions was grown using thermal evaporation method. The effects of different metallic additions and annealing at a temperature below the glass transition temperature  $T_g$  on the optical characteristics was explored. The bulk and thin films of the samples were tested by x-ray diffraction, which reveals that are amorphous. The optical energy gap  $E_0$  was found to decrease with the addition of metal, the amount of decrease depends on the chemical character of added metal. Annealing leads to a decrease of the optical energy gap with annealing time. The gamma irradiation (up to 100 kGy rad) has no detectable effect on the optical energy gap.

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### 1. INTRODUCTION

Recent investigations on chalcogenide glasses are mainly concerned with electrophysical, optical and structural properties as a function of composition[1]. The importance of these glasses is associated with their interesting optical properties and their possible applications as optical fibers[2-3], x-ray imaging [4], optical fibers, lasers [5-6] etc. where linear and non linear optical properties of glasses are of main concern [7-9]. Optical linear characterization of a material requires not only the values of both the refractive index and absorption coefficient at a specific wavelength but also their evolution as a function of the optical wavelength [10].

Chalcogenide glasses are known to have flexible structure, in the sense that each atom can adjust its neighboring environment to satisfy the valance requirements. There is a strong experimental evidence [11-12] that many metal atoms, such as Cu, are incorporated in chalcogenide glasses at tetrahedral sites. Based on the covalent nature of the local bonding models of these glass structures suggest that the chalcogen atoms also exist at tetrahedral sites when the metal concentrations are large enough.

Study of the optical properties of chalcogenide glasses is very important for the determination of the electronic band structure as well as other optical parameters, such as optical energy gap and refractive index. Optical absorption in solids can occur

in several mechanisms. There is no pronounced feature of the optical absorption spectrum that can be directly related to the optical gap. For crystalline semiconductors, the associated optical absorption spectrum terminates abruptly at the fundamental gap, while in amorphous semiconductors a tail in the absorption spectrum encroaches into the gap region. This tail in the optical absorption spectrum, arising as a consequence of the tail and gap states, makes the optical gap of an amorphous semiconductor difficult to define experimentally. In the high-absorption region (where absorption is associated with interband transitions), the form of the absorption coefficient  $\alpha(\omega)$  was given in quadratic form by Tauc [13] and by using the equation of the form

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^n / \hbar\omega \quad (1)$$

Where  $n = 1/2$  or  $3/2$  depending on whether the transition is allowed direct transition or forbidden indirect transitions,  $\alpha(\omega)$  is the absorption coefficient,  $E_{\text{opt}}$  is the optical band gap and  $B$  is a constant. Fundamental absorption edge in most amorphous semiconductors follows an exponential law [14]. The absorption coefficient of any amorphous semiconductor has been observed to obey an equation similar to Eq.(1).

Among the quaternary compounds, the pseudo-binary alloys (CuIn)(SeTe) and (CuIn)(SeS) are of potential interest as promising materials for photovoltaic solar energy conversion devices since the band gaps of these compounds are well adapted to the solar spectrum [15]. In this article, a correlation between the added metal type and the variation in some physical parameters is established. The effect of annealing at a temperature just below the glass transition temperature at different times on the optical parameters is investigated.

## 2. EXPERIMENTAL

Se-Te amorphous semiconducting alloy was prepared by taking the 99.999% pure elements and quantities were adjusted to the required composition. The silica tube containing the contents was evacuated to  $10^{-5}$  Torr and sealed under vacuum. The glassy material was prepared by heating the silica tube at  $850^\circ\text{C}$  for 20h. During heating the tube was regularly rocked to ensure good mixing of the constituents. The melt was suddenly quenched in ice-water mixture to prevent any possible crystallization upon solidification. Different metals like Cu, Ag (transition metals) and Sn (poor metal) were added in the proper ratios to the previously prepared  $\text{Se}_8\text{Te}_2$  alloy using the melt quenching technique. Silver has the highest electrical and thermal conductivity for a metal and tin is a silvery, malleable poor metal that is not easily oxidized in air and resists corrosion. The ingredients were placed in clean and dry silica tubes and then sealed under a vacuum of  $10^{-5}$  torr. The tubes were placed in a high temperature furnace at  $850^\circ\text{C}$  for other 20 hours then quenched as before. Thin film samples were grown by thermal evaporation method using an Edwards E-306 coating unit. Films of 2000 Å thicknesses were grown on clean glass substrates kept at room temperature during the growth process under a vacuum of  $10^{-6}$  torr. The growth rate was maintained as low as  $10 \text{ \AA/s}$  during the growth process. Amorphous nature of bulk and the deposited films were confirmed using x-ray diffraction and composition was examined using an energy dispersive x-ray, EDX, unit attached to a Joel scanning electron microscope. The films were found to have similar composition as the bulk material within  $\pm 10\%$ .

For all the prepared thin film samples, optical absorption and transmission were measured using a double beam spectrophotometer type UV/VIS Shimadzu-160A in the spectral range from 200-1100nm. The optical absorption and transmission of thin film samples were repeated and it found within error  $\pm 15\%$ .

The concept of the small polaron ( $r_p$ ) is well known. The excess electron so distorts the surrounding lattice that the potential well thereby generated is deep enough to induce localization. Polarons have been studied in ordered and disordered solids (16). Bogomolov et al. (17) find that,

$$r_p = 1/2(\pi/6N)^{1/3} \quad (2)$$

where N is the number of sites per unit volume.

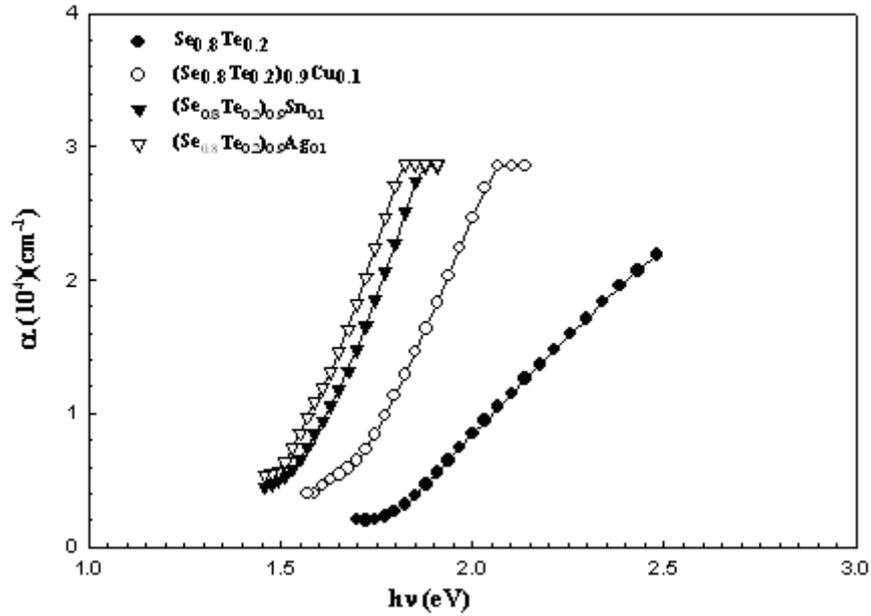
The thin film samples were irradiated with gamma ray exposure up to 100 kGy rad in the National Centre for Radiation Research and Technology, Egyptian Atomic Energy Authority.

### 3. RESULTS AND DISCUSSION

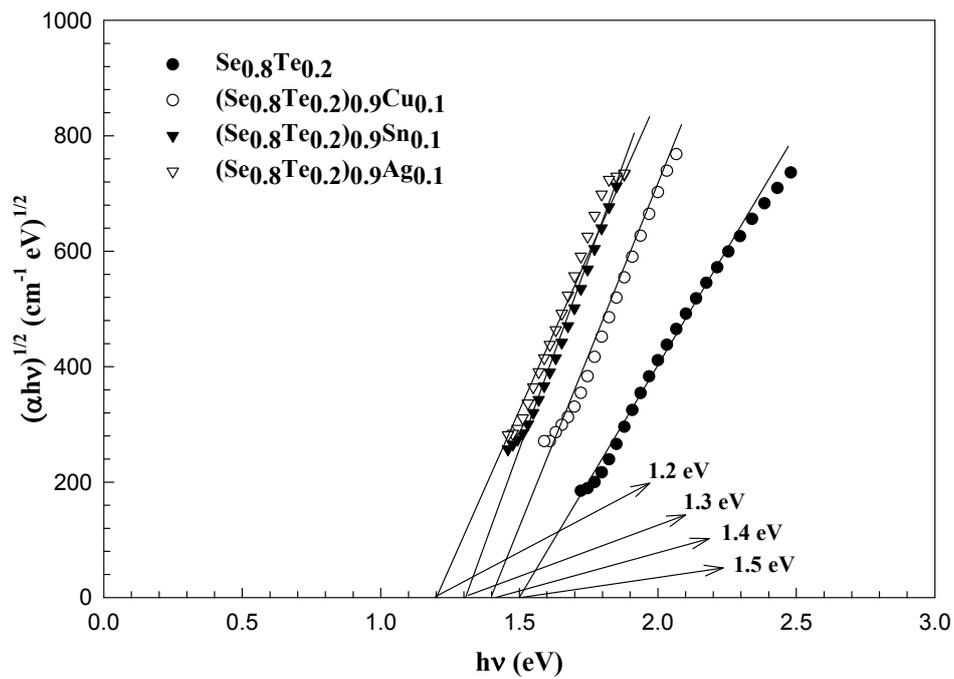
X-ray diffraction analysis was performed for bulk and thin films samples of the prepared compositions. No peaks, characteristic to the crystalline phase, were detected in the obtained patterns and hence confirming the amorphous nature of the prepared samples. The physical values of the glass bulk density,  $\rho_g$ , the molar volume, V, the calculated concentration of Cu, Ag, Sn atoms in the glass, the small-polaron radius,  $r_p$ , the average space R of metal atoms in the glass as explained in (16), and the coordination number were calculated. For ternary glasses both  $\rho_g$  and V depended on the metal concentration. The change in V was due to the change in structure caused by the variation in interatomic spacing, which could be attributed to the change in the number of bonds per unit volume of the glassy network. The value of  $\rho_g$  increase 5%, 6% and 1% for adding Cu, Ag, and Sn respectively as shown in Table 1. So, the molar volume of the ternary glass system would be higher than the binary Se<sub>0.8</sub>Te<sub>0.2</sub> glass, as shown in Table 1. The graphs of absorption coefficient  $\alpha$ ,  $(\alpha h\nu)^{1/2}$  and  $\ln(\alpha)$  against photon energy  $h\nu$  for materials in the system (Se<sub>0.8</sub>Te<sub>0.2</sub>)<sub>0.9</sub>M<sub>0.1</sub> is shown in Figs. 1, 2 and 3.

Table 1 Glass composition system, densities ( $\rho$ ), molar volumes (V), the concentrations of metals atoms per unit volume (N), the average spacings of metals atoms (R), the small-polaron radii( $r_p$ ) deduced from the density and the average coordination number(C).

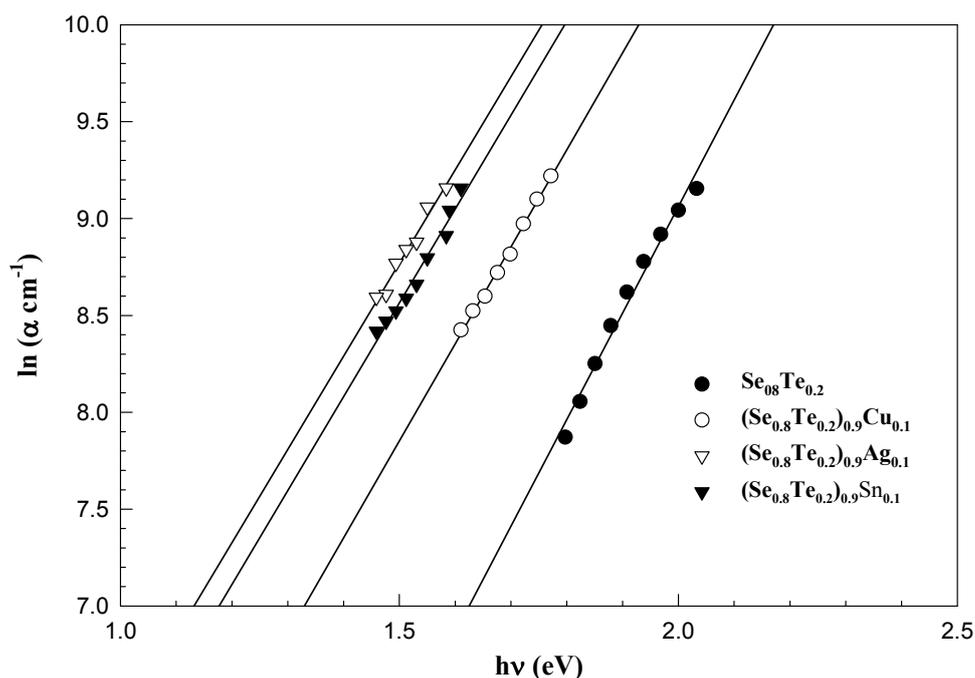
Composition system	$\rho_g$ (g cm <sup>-3</sup> )	V (cm <sup>3</sup> )	N x 10 <sup>21</sup> (cm <sup>-3</sup> )	R (Å)	$r_p$ (Å)	C
Se <sub>0.8</sub> Te <sub>0.2</sub>	5.04	17.59	----	----	----	2.0
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Cu <sub>0.1</sub>	5.27	20.91	5.00	5.85	2.36	2.1
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Ag <sub>0.1</sub>	5.32	20.02	2.94	6.98	2.81	2.2
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Sn <sub>0.1</sub>	5.11	21.05	2.68	7.20	2.90	2.2



**Fig.1:** Absorption coefficient ( $\alpha$ ) against photon energy ( $h\nu$ ) for thin film of all systems



**Fig.2** The variation of the  $(\alpha h\nu)^{1/2}$  with photon energy ( $h\nu$ ) for thin films of all systems.



**Fig. 3.** The variation of the  $\ln\alpha$  with photon energy ( $h\nu$ ) for thin films of all systems.

The following points may be noted:

- 1- There is no sharp absorption edge, and this is a characteristic of the glassy state that is consistent with those obtained from [18].
- 2- The position of the fundamental absorption edge shifts to lower energy with increasing metal content.
- 3- For the glasses in the system  $(\text{Se}_{0.8}\text{Te}_{0.2})_{0.9}\text{M}_{0.1}$  there is a distinct evidence of an additional absorption mechanism near the absorption edge. In attempting to explain the origin of this feature we have suggested that for these glasses a sub-band, associated with the presence of metal, projects into the pseudo-gap at the edge of the valence band; this sub-band may have a tail of states due to compositional disorder [18].
- 4- The value of B in Eq. (1) can be determined from the slope of the linear part of curves showing  $(\alpha h\nu)^{1/2}$  against  $(h\nu)$  in Fig. 2. These values are found and listed in Table 2. It is found that the value of B ( $\text{cm}^{-1/2}\text{eV}^{-1/2}$ ) decreases with adding metal contents (Cu, Ag and Sn).
- 5- Fig 3 shows the variation of  $\ln(\alpha)$  with photon energy ( $h\nu$ ) for  $(\text{Se}_{0.8}\text{Te}_{0.2})_{0.9}\text{M}_{0.1}$  glasses. The value of  $\Delta E$  are calculated from the slope of the straight line of these curves, and are given in Table 2.

Table 2. The dependence of Optical energy gap  $E_{opt}$ , the constant  $B$  and the width of the tail of the localized states in the band gap  $\Delta E$ , on the additive metals to the binary system  $Se_{0.8}Te_{0.2}$ .

Composition system	$E_{opt}$ (eV)	$B \times 10^5$ ( $cm^{-1}eV^{-1/2}$ )	$\Delta E$ (eV)
$Se_{0.8}Te_{0.2}$	1.50	0.72	0.18
$(Se_{0.8}Te_{0.2})_{0.9}Cu_{0.1}$	1.40	0.63	0.20
$(Se_{0.8}Te_{0.2})_{0.9}Sn_{0.1}$	1.30	0.55	0.21
$(Se_{0.8}Te_{0.2})_{0.9}Ag_{0.1}$	1.20	0.51	0.21

- 6- The value of  $E_{opt}$  decreases with adding metal content as shown in Table 2. It is assumed that in the process of absorption the incident photon excites electron from states near (above and below) the top of the valence band to states near the bottom of the conduction band, i.e. across the pseudo-gap. As already noted, Mott and Davis [19] in discussing inter-band absorption have considered the situation where the matrix element for electronic transitions is taken as constant. It is assumed that as the density of states in the sub-bands increases (corresponding to increasing concentration of metals (Cu, Ag, Sn), the density of states in the main bands decreases. This effect may be also due to the change in bond angles and/or bond lengths.
- 7- Gamma doses up to 100kGy rad have no detectable effect on the optical energy gap. Our results are contradict the effect of gamma radiation on the optical energy gap of oxide glass [20], cellulose nitrate polymer [21] and the compounds, CuInTeSe, CuInSeS and CuInTeS [22].

The lone-pair electrons adjacent to electropositive atoms will have higher energies than those close to electronegative atoms. Thus, the addition of electropositive elements to the chalcogenide alloy may raise the energy of some lone-pair states sufficiently to broaden further band to the inside of the gap. This stability to  $\gamma$ -radiation can be connected with the fact that this kind of radiation does not excite the upper valence electrons, e. g., lone-pair electrons forming the valence band in chalcogenides, but electrons which have lower energy, e.g.,  $\sigma$ -electrons forming interatomic bonds.

It can be seen from Table (2) that the energy gap of  $(Se_{0.8}Te_{0.2})_{0.9}Sn_{0.1}$  is less than of  $(Se_{0.8}Te_{0.2})_{0.9}Cu_{0.1}$  as Sn is more electropositive than Cu and hence the effect of Sn in narrowing of the gap is expected to be more than that of Cu. The obtained results were found to agree with the results of references [23-26].

Table (3) shows the variation between optical energy gap and annealing times (hrs) with adding different metals to SeTe system. As clear from Table (3), the optical energy gap for each system was found to decrease with the increase of annealing time (hrs).

Table 3. Optical energy gap  $E_{OPT}$  at different annealing periods below softening temperature ( $T_g$ ) for thin films of composition systems

Compositions System	$T_g$ °C	Annealing periods(hrs).					
		24	48	72	96	120	144
Se <sub>0.8</sub> Te <sub>0.2</sub>	68	1.45	1.20	1.15	1.10	1.10	1.10
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Cu <sub>0.1</sub>	76	1.20	1.10	1.05	1.05	1.05	1.05
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Ag <sub>0.1</sub>	90	1.15	0.90	0.85	0.80	0.80	0.80
(Se <sub>0.8</sub> Te <sub>0.2</sub> ) <sub>0.9</sub> Sn <sub>0.1</sub>	71	1.20	0.95	0.95	0.90	0.90	0.90

This decrease in  $E_{opt}$  continues down to certain value where it reaches the saturation. The decrease in  $E_{opt}$  with annealing time can be explained in the following sequence:

- heat treatment (at a temperature just below  $T_g$ ) is expected to increase randomness in the structure and hence increase the density of localized states with a consequent increase in the transition probabilities.
- increase of the transition probabilities leads to narrowing of the band gap.

#### 4. CONCLUSIONS

We have studied the effect of adding Cu, Ag and Sn on the optical properties of Se<sub>0.8</sub>Te<sub>0.2</sub> amorphous chalcogenide system concluded that:

- 1- Absorption coefficient increases with the addition of metals to Se<sub>0.8</sub>Te<sub>0.2</sub> system.
- 2- Absorption coefficient of (Se<sub>0.8</sub>Te<sub>0.2</sub>)<sub>0.9</sub>Sn<sub>0.1</sub> system lies nearly down to the (Se<sub>0.8</sub>Te<sub>0.2</sub>)<sub>0.9</sub>Ag<sub>0.1</sub> system.
- 3- Optical energy gap decreases with the addition of metals Cu, Ag and Sn to Se<sub>0.8</sub>Te<sub>0.2</sub> system.
- 4- Heat treatment at temperature below  $T_g$  causes lowering of optical band gap with time (hrs).
- 5- Gamma radiation doses up to 100 kGy rad have no detectable effect on the optical energy gap.

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