Study the Physical Properties of Some Alloy Materials and Effect of Gamma Radiation

H.H.Amer[1],

[1]Solid State Department, National Center for Radiation Research and Technology Nasr City, Cairo, Egypt

S.Ebraheem[2], K.E.Ghareeb[3], F.A.Eissa[4], S.Eid[2], N.M.Abdel-kader[2]

[2]Dosimerty Department, National Center for Radiation Research and Technology   Nasr City, Cairo, Egypt

[3]Metallurgy Department, Nuclear Research Center, AEA, Cairo, Egypt

[4]Chemistry Department, Faculty of Science, Menoufiya University, Cairo, Egypt

Abstract

The present paper reports the effect of replacement of selenium by tellurium on the optical gap and some other physical parameters of new quaternary chalcogenide $Te_xGe_{20}Se_{(60-x)}As_{20}$ (x = 0, 10, 15 and 20 at. %) thin films. Thin films with thickness 100 nm of $Te_xGe_{20}Se_{(60-x)}As_{20}$ were prepared by thermal evaporation of the bulk samples. Increasing tellurium content is found to affect the average heat of atomization, cohesive energy and energy gap of the $Te_xGe_{20}Se_{(60-x)}As_{20}$ alloys. Optical absorption measurements showed that the fundamental absorption edge is a function of composition. The optical absorption is due to allowed direct transition and the energy gap decreases with the increase of tellurium content. The chemical bond approach has been applied successfully to interpret the decrease of the optical gap with increasing tellurium content. it has also been observed that the increase of Te was followed by decrease in glass transition temperature. The prepared films were irradiated by gamma rays at doses up to 200kGy. It was found that the compositions were almost stable against gamma radiation.

Keywords: amorphous, chalcogenide, optical properties.

1. Introduction

Alloy materials are substances composed of two or more elements. In our study we toke chalcogenide glasses as an example for the alloy. Chalcogenide glasses are a recognized group of inorganic glassy materials which always contain one or more of the chalcogen element S, Se ,or Te, in conjunction with more electro negativity elements as Sb, As and Bi. Chalcogen glasses are generally less weakly bonded materials than oxide glasses [1].

Chalcogenide glassy semiconductors have been the subject of considerable attention due to their interesting optical properties and technological applications, like optical imaging or storage media and especially in the fields of infrared optical transmitting materials, fiber optics and memory device[2]

The absence of long–range order of chalcogenide glassy semiconductors allows the modification of their optical properties to a specific technological application by continuously changing their chemical composition. Hence the study of the dependence of the optical properties on composition is important to improve technological application.

The present study is undertaken in order to investigate the influence of addition of tellurium (0, 10, 15 and 20 at. %), which is higher in atomic weight (more electropositive) than selenium on the optical properties of the new amorphous $Te_xGe_{20}Se_{(60-x)}As_{20}$ thin films. In addition, the optical band gap (E_g), the average heat of atomization (H_s) and the cohesive energy (CE) of the $Te_xGe_{20}Se_{(60-x)}As_{20}$ glasses have been examined theoretically.

2. Experimental procedures

$Te_xGe_{20}Se_{(60-x)}As_{20}$**(where x=0, 10, 15and 20 at%)** films were prepared using the melt-quenching technique. The constituent elements Ge, As, Se and Te (99.999%purity) were weighed and mixed in the appropriate stoichio-metric proportion and sealed in evacuated (10^{-5}torr) silica tubes. These tubes were then placed in a furnace and were heated; stepwise to 900C^o to allow the elements to react completely .The tubes were kept at the maximum temperature for 10h, to ensure that the melt was homogeneous. After quenching in ice water, the alloy was removed by cutting the tubes. The film samples were deposited by the thermal evaporation techniques which were performed inside a coating **(Edward306E)** System at pressure **(10^{-5}torr)** cleaned glass slides with acetone then de-ionized water were used as substrates. The substrates holder was continuously rotated with slow motor and the evaporation rate kept constant to ensure the homogeneity of films .The thicknesses of these films were controlled by using a quartz crystal **(Edward FTM5)** thickness monitor to be about 1000A^O. The elemental compositions of the investigated specimens were checked using the energy dispersive X-Rays spectroscopy. Deviations in the elemental composition of the evaporated thin films from the initial bulk specimens did not exceed 1.0 mol%. The amorphous state of the films was checked using an x-ray diffract meter (Philips type **1710** with **Cu** as a target and **Ni** as a filter) the absence of crystalline peaks confirmed the glassy state of the prepared

samples. Density measurements of the considered samples were made by germanium crystal which was used as reference material for determining the toluene density, $\rho_{tol.}$ The sample density was obtained from the

$$d_{sample} = \frac{W_{air}}{W_{air} - W_{toluene}} \times d_{toluene} \tag{1}$$

Where W is the weight of the sample. For each composition, the experiment was repeated three times to get the average density of the sample (ρ_s). The thermal behavior was also investigated using shimadzu 50 differential scanning calorimeter. About 20 mg of each sample in powdered form was sealed in standard aluminum pan and scanned over a temperature from room temperature to about 773 K at uniform heating rate 8K/min. double beam **(Shimadzu 2101 UV-VIS)** Spectrophotometer was used to measure reflectance and transmittance for the prepared films in the spectral wavelength range 200-1100nm. Gamma irradiation was applied to films with doses up to 15Mrad using the gamma cell of the Co-60 source at the National Center for Radiation Research and Technology ,Cairo ,Egypt.

3. Result and Discussion

Ioffe and Regel[3] have suggested that the bonding character in the nearest neighbor region, which is the coordination number, characterizes the electronic properties of the semiconducting materials. The coordination number obeys the so- called 8-N rule, where N is the valence of an atom; the number of the nearest-neighbor atoms for Ge , As ,Se and Te are calculated and listed in table1. The average coordination number in the quaternary compounds $A_\alpha B_\beta C_\gamma D_\lambda$ is as:

$$(\alpha Nco(A) + \beta Nco(B) + \gamma Nco(c) + \lambda Nco(D)))/(\alpha + \beta + \gamma + \lambda) \tag{2}$$

Where: $\alpha, \beta, \gamma, \lambda$ are the valences of the elements of compound .The determination of N_{co} allows the estimation of the number constraints(N_s). This parameter is closely related to the glass-transition temperature and associated properties. For a material with coordination number N_{co}, N_s can be expressed as the sum of the radial and angular valence force constraints.[4]

$$N_S = \frac{N_{CO}}{2} + (2N_{CO} - 3) \tag{3}$$

The calculated values of N_{co} and N_s for the $Te_x Ge_{20} Se_{(60-x)} As_{20}$system are given in table2. The parameter r, which determines the deviation of stoichiometry and is expressed by ratio of the covalent bonding possibility of chalcogen atoms to that non-chalcogen atoms, was calculated using the following relation :[5,6]

$$r = \frac{(60-x)N_{co}(Se)}{20 N_{co}(Ge) + 20 N_{co}(As) + x N_{co}(Te)} \tag{4}$$

The calculated values of r for the $Te_x Ge_{20} Se_{(60-x)} As_{20}$ Films are given in Table2.According to Pauling [7] the heat of atomization $H_s(A-B)$ at standard temperature and pressure of a binary semiconductor formed atoms A and B is the sum of the heats of formation ΔH and the average of the heats of atomization H_S^A and H_S^B corresponding to the average non-polar bond energy of the two atoms[8,9]:

$$\Delta H\ \alpha\ (\chi_A - \chi_B) \tag{5}$$

Proportional to the square of the difference between the electro-negativities χ_A and χ_B of the two atoms:

$$H_s(A - B) = \Delta H + \frac{1}{2}(H_s^A + H_s^B) \tag{6}$$

In most cases the heat of formation of chalcogenide glasses is unknown, the heat of formation ΔH is about 10% of the heat of atomization and, therefore, can neglected. To extend the idea to ternary and higher order semiconductor compounds ,the average heat of atomization is defined for a compound $A_\alpha B_\beta C_\gamma D_\lambda$ as[10,11]:

$$H_s = \frac{\alpha\ H_s^A + \beta\ H_s^B + \gamma\ H_s^C + \lambda\ H_s^D}{\alpha + \beta + \gamma + \lambda} \tag{7}$$

Values of H_S of Ge , As , Se and Te are given in table2. As shown in table2,the values of H_S decrease with increasing Te content. To correlate H_S with E_g in non crystalline solids, it is reasonable to use the average coordination number instead of the iso-structure of crystalline semiconductors. It was found that the variation in the theoretical values of the energy gap ($E_{g,th}$)with composition in quaternary alloys can be described by the following simple relation[12]:

$$E_{g,AB}(Y)= YE_{gA} +(1-Y)E_{gB} \qquad (8)$$

Where, Y is the volume fraction of element. For quaternary alloys:

$$E_{g,\ th}(ABCD) = a\ E_g(A)+b\ E_g(B)+c\ E_g(C)+d\ E_g(D) \qquad (9)$$

Where a, b ,c and d are the volume fractions of the elements A, B, C and D Respectively. $E_g(A)$, $E_g(B)$, $E_g(C)$ and $E_g(D)$ are the corresponding optical gaps. The conversion from a volume fraction to atomic percentage is made using the atomic weights and densities tabulated in table1[13].The calculations of ($E_{g,th}$) based on the above equation for the $Te_xGe_{20}Se_{(60-x)}As_{20}$ Films, are given in table2, which reveals that the addition of Te led to change in the considered properties. The bond energies of films were listed in table 3. By increasing the Te content, the average bond strength of the compound decrease and hence E_g will decrease. **Fig.1** shows the x-ray diffraction patterns for $Te_xGe_{20}Se_{(60-x)}$ As_{20} thin films. The absence of diffraction lines in the x-ray patterns indicates that the films have amorphous structures. Transmission spectra, corresponding to amorphous Te_x Ge_{20} $Se_{(60-x)}$ As_{20} thin films before and after radiation of 1and 200KGy are plotted in figs.2, [a,b] and 3 shows a clear ultraviolet shift of the interference free region with increasing Te content.

3.1 Optical Energy gap
For the optical energy gap in which the minimum of the conduction band and the maximum of the valence band, applying Mott and Davis model, $\alpha(\upsilon)h\upsilon=B(h\upsilon-Eopt)^n$ the absorption edge coefficient $\alpha(\upsilon)$ is function of photon energy[13]. $(\alpha h\upsilon)^n$ is plotted for different n versus $(h\upsilon)$. The extrapolations of the lines of $(\alpha h\upsilon)^{1/2}=0$ gives the optical energy gap. The best line was obtained for the indirect allowed optical band gap for all the studied films Fig(7) the indirect optical band gap (E_g), which was evaluated from the linear plots of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ .The optical absorption coefficient (α) for indirect transition was given by (α) was given by Fahrenbruch and Bube [14]

$$\alpha\ (h\upsilon) = A\ (\ h\upsilon\ - E_{opt})^n \qquad (10)$$

Where A is constant, h is Plank′s constant, υ is the frequency of the radiation, E_{opt} is the optical energy gap, and n, is a number which characterizes the optical absorption processes, n=1/2, 1, 3/2, 2, 3 according to direct and non-direct transition depending on the nature of the electronic transition responsible for the   absorption n=1/2 for allowed direct transition. n=3/2 for the forbidden indirect transition. And n=2 refers to indirect allowed transitions. The absorption coefficient for direct transition takes the values from 10^4 to10^5 cm^{-1},while the absorption coefficient for indirect transition takes the values from 10 to 10^3 According to Urbach rule [15], the absorption coefficient, α, can be calculated as follows:

$$\alpha = \frac{1}{L}\ln I_o/It \qquad (11)$$

Where, I_o and I_t are the intensities of the incident and transmitted light, respectively, L is the thickness of the sample (cm). The present results were found to obey equation (10) with r=1/2 for all films. This   indicates direct allowed transitions. Values of absorption coefficient were taken between10^4 to 10^5 cm^{-1}.   **Figurers (4.a) and (4.b)** are a best fit of $(\alpha h\upsilon)^{1/2}$ versus photon energy $(h\upsilon)$ for $Te_xGe_{20}Se_{(60-x)}$ As_{20} thin films before and after radiation of 1and 200 KGy. The intercepts of the straight lines with the photon energy axis give the values of the optical band gap.

The variation in E_g as a function of Te content before and after radiation of 1 and 200 kilo-gray are shown in fig 5. It is clear that E_g decreases with increasing Te content of the investigated films. Fig 6 shows the density of amorphous Te_xGe_{20} $Se_{(60-x)}$ As_{20} and it is clear that density increases with increasing Te content. The possible bond distribution at various compositions using chemically ordered network (CNO) model. This model assumes that :a) Atoms combine more favorably with atoms of different kinds than with the same and b)bonds are formed in the sequence of the bond energies. The bond energies D (A-B) for   hetero-nuclear bonds have been calculated by using the empirical relation:

$$D\ (A-B) = [\ D(A-A).D(B-B)]^{1/2} + 30\ (\chi_A - \chi_B)^2 \qquad (12)$$

Proposed by Pauling, where D (A-A) and (B-B) are the energies of the homo-nuclear bonds (in units of Kcal/mol); χ_A and χ_B are the electro negativities for the involved atoms [16]. Knowing the bond energies, we can estimate the cohesive energy (CE), i.e. the stabilization energy of an infinitely large cluster of the materials per atom, by summing the bond energies over all the bonds expected in the system under test. The CE of the prepared samples is evaluated from the following equation [17].

$$ CE = \sum (C_i D_i / 100) \tag{13} $$

Where, C_i and D_i are the number of the expected chemical bonds and, the energy of each corresponding bond. The calculated values of CE for all compositions are presented in table 2. With the exception of $Te_xGe_{20}Se_{(60-x)}As_{20}$ glass, CE decreases with increasing Te content. Increasing the Te content leads to an increase in the average molecular weight. This increases the rigidity (strength) of the system. The decrease in the optical band gap with increasing Te content can be interpreted via the chemical-bond approach, used successfully by Bicerano and Ovshinsky to explain the electrical behaviour of amorphous systems.This approach explains the behaviour in the terms of the cohesive energy(CE). It allows the determination of the number of possible bonds and their type(heteropolar and homopolar). The authors assumed that :

a)atoms combine more easily with atoms of a different rather than the same type.

b)Bonds are formed in the sequence of decreasing bond energy until all the available valencies urateatof the atoms are saturated.

c)each constituent atom is coordinated by 8-N atoms, where N is the number of outer shell electrons and this is equivalent to neglecting the dangling bonds and the other valence defects.The energies of various possible bonds in the $Te_xGe_{20}Se_{(60-x)}As_{20}$ system are given in table 3. Depending on the bond energy(D), The chemical bond approach could be applied to the present system For Samples containing "Te" content ,Ge,As and Se atoms bond toSe atoms to form GeSe ,AsSe and TeSe structural unit, respectively. After forming these bonds, there are still "Se" valencies which must be satisfied by formation of Se-Se bond (Se chains) For $Te_xGe_{20}Se_{(60-x)}As_{20}$, which represents the So-called Stoichiometric composition. This glass is composed of completely cross–linked structural units of Ge Se , AsSe and Te Se with out any excess "Se" in the system. The effect of gamma radiation with different doses from 0 to200KGy on the four compositions is shown in table 4.The results indicated that the prepared films were almost stable against radiation. However , there was aslight change in E_{opt} when gamma doses were increased in the different "Te" content.

4. Conclusion

Optical data indicated that the allowed direct gap is responsible for photon absorption in $Te_xGen_{20}Se_{(60-x)}As_{20}$ thin film. Increasing Te content at the expense of Se atoms decrease the optical gap of the films. The values of heat of atomization,coordination number, number of constrains and cohesive energy for $Te_x Ge_{20} Se_{(60-x)}As_{20}$ depend on the glass composition. The increase in Te content leads to a decrease with in $E_{g,th}$ and H_s/N_{co}. Cohesive energy decreases with the increase in Te content.The chemical-bond approch can be applied successfully to interpret the decrease in the optical gap with increasing Te content. It has also been found that the compositions were almost stable against gamma radiation at doses up to 200KGy.

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Table1.

Physical characteristics	Ge	Se	As	Te
Energy gap(ev)	0.95	1.95	1.15	0.65
Density(g/cm3)	5.3	4.79	4.7	6.24
Coordination no.	4	2	3	2
Bond energy(kcal/mol)	37.6	44.02	32.1	33
Hs(kcal/mol)	90	54.17	69	46
Electro negativity	2.01	2.4	2.18	2.1
Radius(pm)	122	115	119	140

Table (1) shows values of the optical band gap, density, coordination number, heat of atomization (H$_s$), bond energy and electro negativities of Ge, Se, As and Te respectively which are used for calculations.

Ratio	Composition	N$_{co}$	N$_s$	r	H$_s$ (kcal/mol)	H/N$_{co}$	E$_{g,th}$ (ev)	E$_{g,exp}$ (ev)	d$_{th}$ (g/cm^3)	d$_{exp}$ (g/cm^3)	CE (ev/atom)
0 %	Ge$_{20}$As$_{20}$Se$_{60}$	2.6	3.5	0.857	64.302	24.73	1.59	1.63	4.865	4.93	4.43
10%	Te$_{10}$Ge$_{20}$As$_{20}$Se$_{50}$	2.6	3.5	0.625	63.485	24.42	1.46	1.61	4.983	5.15	4.34
15%	Te$_{15}$Ge$_{20}$As$_{20}$Se$_{45}$	2.6	3.5	0.529	63.076	24.26	1.39	1.60	5.043	5.32	4.29
20%	Te$_{20}$Ge$_{20}$As$_{20}$Se$_{40}$	2.6	3.5	0.444	62.668	24.10	1.33	1.59	5.106	5.53	4.24

Table2.

Table (2) Some physical parameters as function of Te content for Te$_x$Ge$_{20}$Se$_{(60-x)}$As$_{20}$ (where x=0 ,10 ,15 , at. 20 %) Films.

Table3.

Bond	Bond energy
Ge-Se	49.4
Se-Se	44.02
As-Se	41.7
Se-Te	40.87
Ge-Ge	37.6
Ge-As	35.61
Ge-Te	35.46
Te-Te	33.1
As-Te	32.7
As-As	32.1

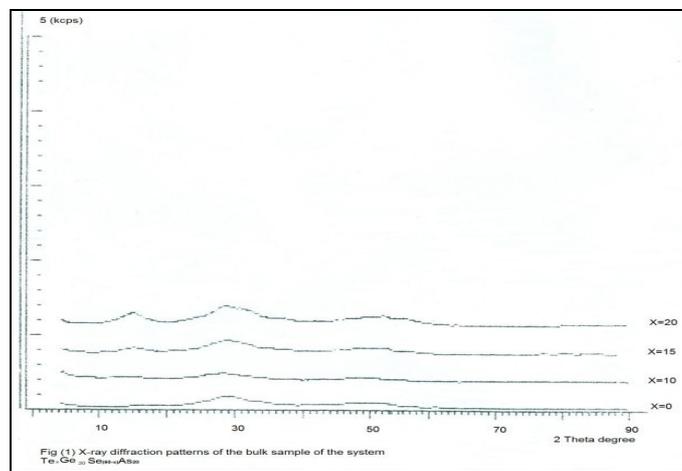**Table (3)** bond energy of formation of various bonds in $Te_x Ge_{20} Se_{(60-x)} As_{20}$ Films .

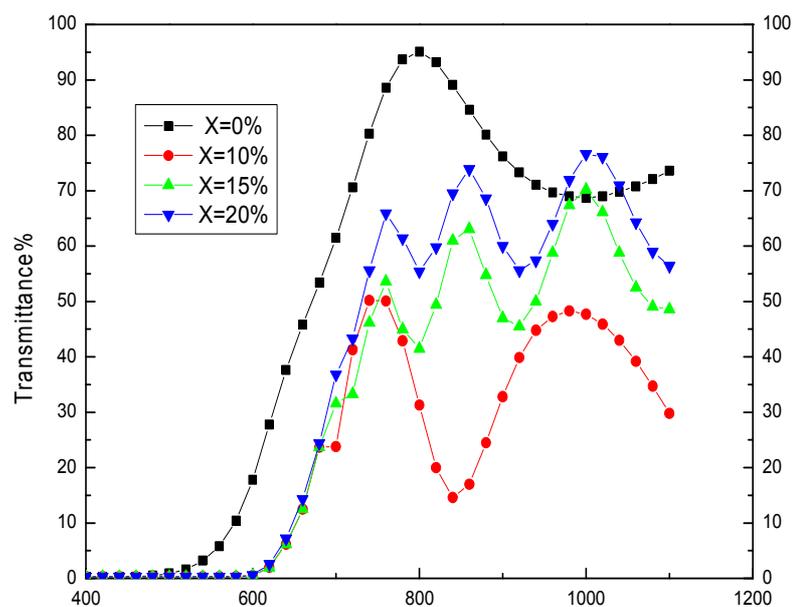**Figure (1)** X-ray diffraction patterns of the amorphous $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) glasses.

Figure (2-a) Transmission spectra of $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) as deposited thin film.
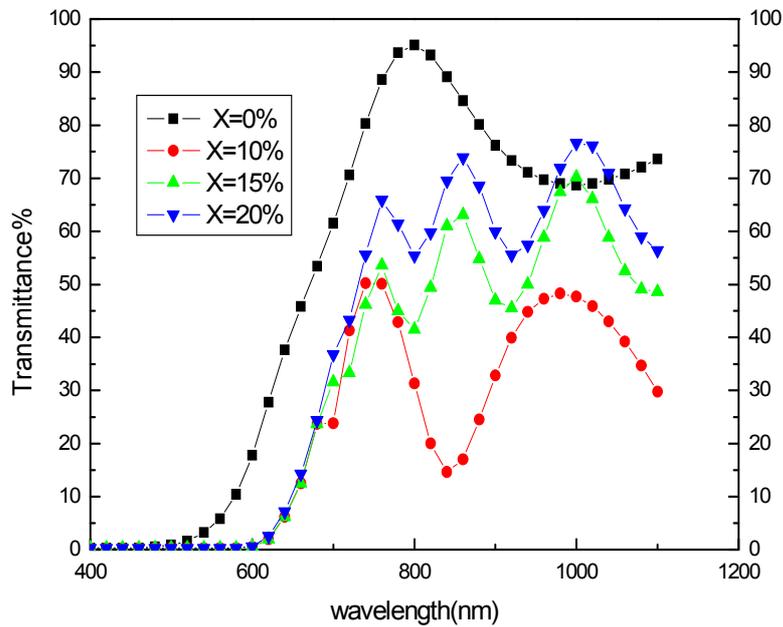
Figure (2-b) Transmission spectra of $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %)   irradiated (with gamma rays) thin film.
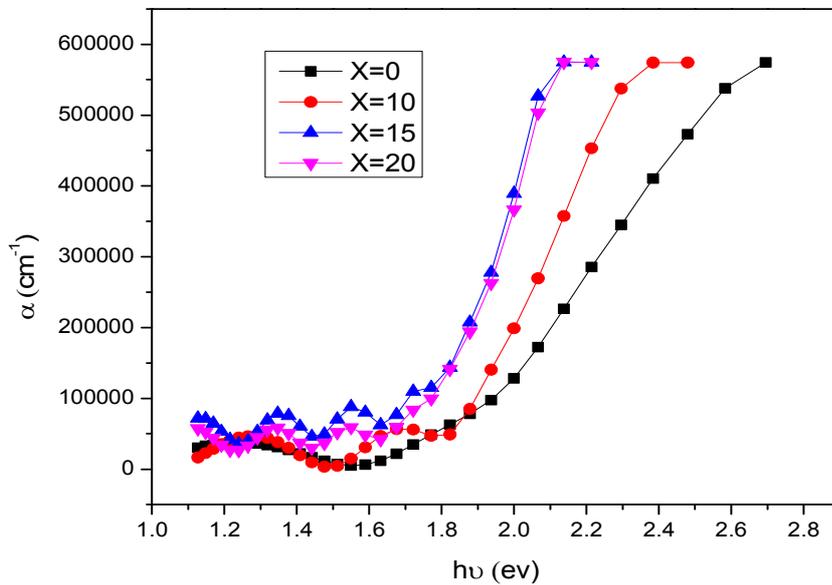
Figure (3) Spectral dependence of the absorption coefficient (α) for $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) as deposited thin films.
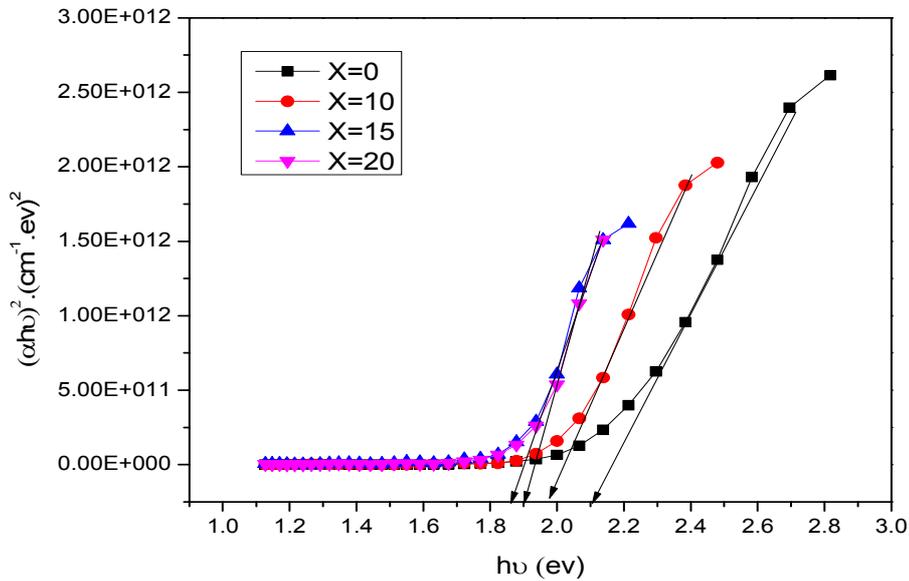
Figure (4-a) Dependence of $(\alpha h\nu)^2$ on photon energy, $h\nu$, for the as deposited $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) thin films, from which the optical band gap, E_g, is estimated (Tauc extrapolation).
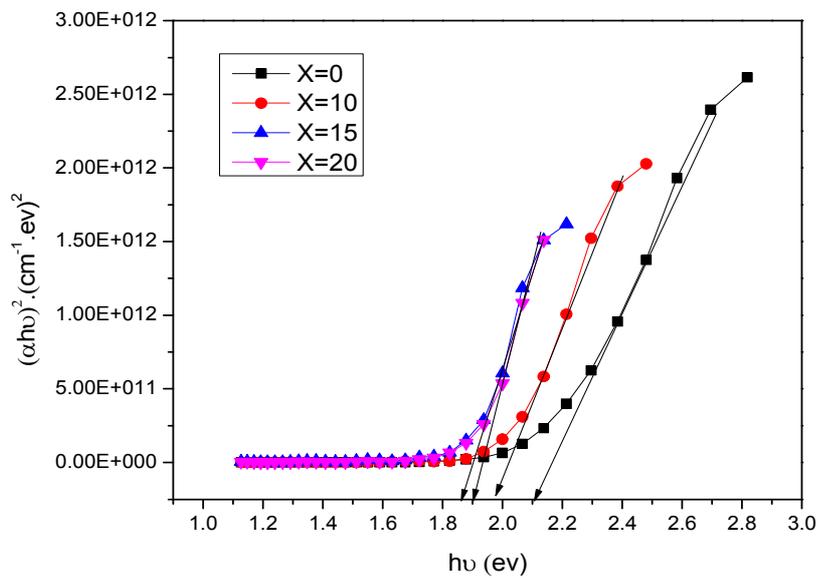
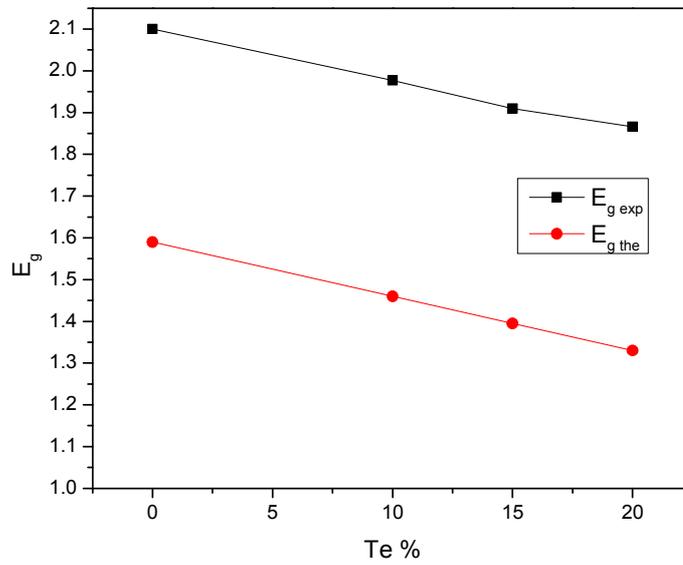**Figure (4-b)** Dependence of $(\alpha h\nu)^2$ on photon energy, $h\nu$, for the gamma irradiated $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) thin films, from which the optical band gap, E_g, is estimated (Tauc extrapolation).

Figure (5) Variation in the optical band gap, E_g, as a function of Te content for $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) thin films.

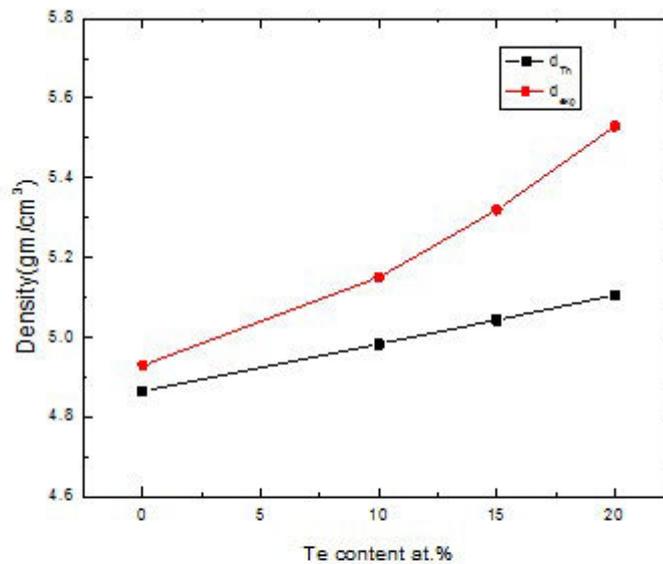**Figure (6)** Compositional dependence of the density for $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) glasses.
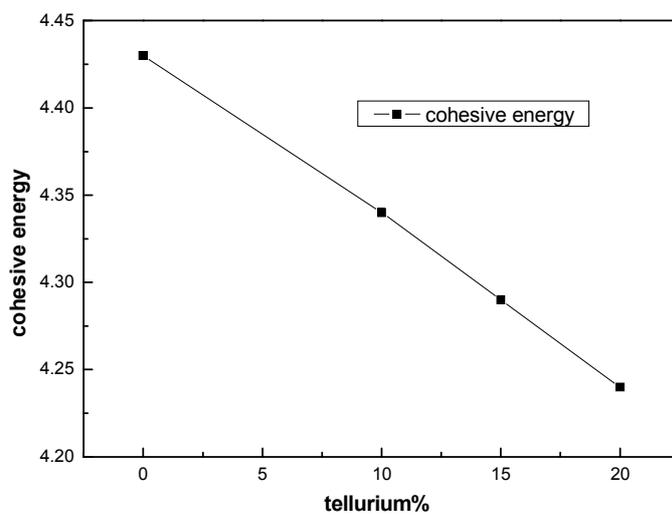
Figure (7) Cohesive energy versus Tellurium% for $Te_xGe_{20}Se_{(60-x)}As_{20}$ (where x = 0, 10, 15 and 20 at. %) glasses.

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