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PHYSICAL BEHAVIOR OF As-Se-Se GLASSES WITH CONSTANT COORDINATION NUMBER (NC = 2.2)

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The present work deals with the effect of S additions on glass density, molar volume, compactness and optical properties of Different compositions of $As_{0.20}Se_{0.80-x}S_x$ ($0.0 \leq x \leq 0.55\ at.\%$) glasses. The coordination number Se and S atoms is the same $N_{Se} = N_S = 2$. Therefore, the coordination number of the present glasses is constant and equal to 2.2. The glass density, compactness, the Tauc parameter $\sqrt{\beta}$ and the Urbach energy are decrease with the addition of S amount whereas the molar volume and the optical gap are increases. Two stoichiometric glasses were observed. The first at 25 at.% S content with Se-S and As-Se bonds and the second at 55 at.% S content with As-S and Se-S bonds. The obtained results are consistent with each others and well discussed in terms of the chemical bonds and the Mott and Davis model.

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1. Introduction

Recently, chalcogenides have paid great interest because of their excellent physically as well as optically characteristics consequently, their potential technologically applications. Such applications appeared in the procedures of international workshops on amorphous and nanostructured chalcogenide glasses [1]. Among of them the use of these materials As-Se or Se in xerographic process, $Ge_{25}Se_{75}$ in lithographic [2], Ge-Te-Se or Ge-Te in CD compatible erasable disks [3], AsS(-Se) based glasses in sensors [4], $As_{40}S_{60-x}Se_x$ far length of low loss IR transmitting devices with [5], the use of $Bi_{29}Tl_{35}Se_{36}$ and As_2S_3(-Se_3), Ge-S_2(Se_2) for memory switching [6]] and photoinduced phenomena [7, 8] as well as using of $Al_{23}Te_{77}$ for electrical memories[9]. On the other hand, the importance of chalcogenides is due to their relatively ease of their preparation. An example is denoted by pure Se that is known to be the only element capable to produce monotonical glass [10]. Consequentially, chalcogenides may be used as a reference material to developed best understand of the glass nature as well as its specified properties. Furthermore, due to these materials exhibit a continue changes in their multi properties with changing the chemical composition, thus, it is possibly to find a correlation of their observed characteristics in property-composition depending on structure arrangements in these glasses. Like studies concerned by thermally [11], mechanically [12], electrically [13], optically [14] and physico-chemical [15] were reported. The As-Se-S glasses are a chalcogenide system which was studied by many authors

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[16-19]. To be the author knowledge there is no a correlation between some of physical properties like as glass density, index of refraction and distribution of chemical bonds especially at constant coordination number. The present paper aimed to prepare different compositions of As-Se-S with constant coordination number and study the effect of S content on the chemical distribution of bonds, Investigate stoichiometry composition.

2. Experimental details

High purity (99.999%) As, Se and S elements were weighted according to their atomic weight and percentage to prepare As-Se-S glasses with the chemical form $As_{0.20}Se_{0.80-x}S_x$ $0.0 \leq x \leq 0.55\ at.\%$. Further detail of the perpetration method were written here [20]. A rod (2 cm length x 0.9 cm width) for each sample was used to calculate the glass density (δ). The glass compactness (gc) was calculated based on the atomic percent (x_i), the atomic mass (Am), Atomic density i^{th} of every element (δ_i) and the measured glass density (δ) through the following relation [21]:

$$gc = \frac{\sum_i x_i Am_i \delta_i^{-1}}{\sum_i x_i Am_i \delta^{-1}} - 1 \quad (1)$$

The molar volume (Vm) was calculated using the density values through the relation:

$$Vm = \delta^{-1} \sum_i x_i Am_i \quad (2)$$

Thermally evaporation technique has been used to prepared As-Se-S thin films with thicknesses ~ 300 nm. Double beam Jasco-630 spectrometer was used for the measurements of the film absorption in the 300-900 nm spectral range.

3. Results and discussion

The glass density was decreases while the molar volume was increases with increasing sulfur content as shown in Fig. 1. Such behavior is consistent with Eq. 2. Also, with the addition of S content (lower dense atoms) at the expense Se leads to decreasing in the glass compactness which would be expected due to the observed decrease in V_m values. Fig. 2 represents the compositional dependence of the absorption coefficient (α) on the wavelength. It well known that, the absorbance (A_p) was correlated with α values through this relation (A_p = α.t where t is the thickness of the film). As shown in the Figure, the introduction of S removes the absorption edge to short wavelengths (blue shift). Such a shift leads to the decrease in the optical gap (E_g) values. The latter was determined by considering the allowed indirect transition rule [22].

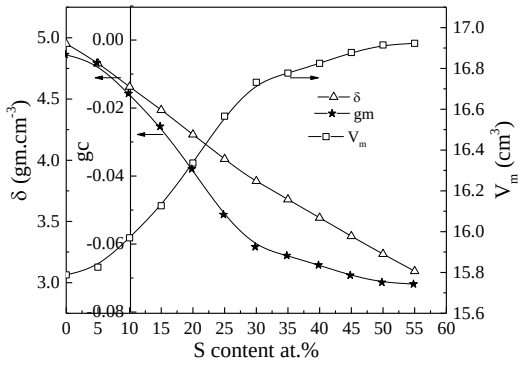

Fig. 1. The glass density, molar volume and compactness vs. S content at.% for $As_{0.20}Se_{0.80-x}S_x$ glasses

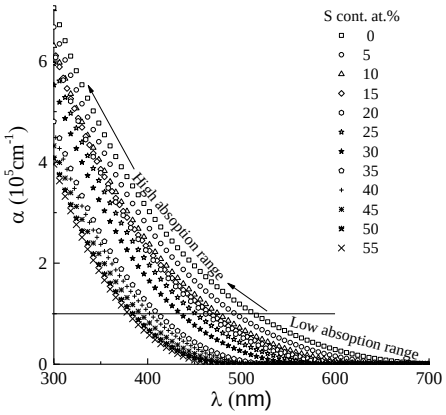

Fig. 2. The absorption coefficient (α) vs. λ for $As_{0.20}Se_{0.80-x}S_x$ films.

According to this rule the square root of the product of absorption coefficient in highly absorption range and incident photon energy $(\alpha.h\upsilon)^{0.5}$ was plotted against $h\upsilon$ as well as represented in Fig. 3. The intersect for each plot in this figure with X-axis gives the of the $\sqrt{\beta}$ and the ration intersect/slope gives the E_g value. The parameter β is an index of refraction dependence parameter ($\beta = 4\pi\sigma_0/(n_0 cE_e$ $where$ σ_0 is the minimal conduction of electricity, n_0 is the static index of refraction, c is the light velocity and E_e is the localized state width) [14]. The deduced value of the $\sqrt{\beta}$ were listed in Table 1.

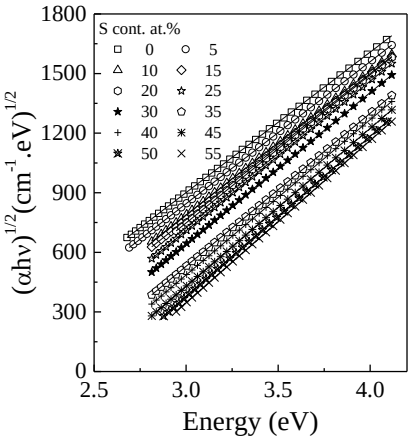

Fig. 3. $(\alpha.h\upsilon)^{0.5}$ vs. hυ for $As_{0.20}Se_{0.80-x}S_x$ films.

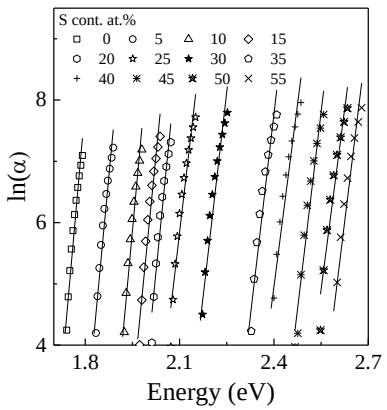

Fig. 4. $ln(\alpha)$ versus hυ for $As_{0.20}Se_{0.80-x}S_x$ films.

On the other hand, Fig. 4 shows the plots of $\ln(\alpha)$ versus $h\upsilon$ for the present films which describe the absorption coefficient dependence on the photon energy ($\alpha = \alpha_0 \exp(h\upsilon/E_e)$ where Ee is the Urbach's energy) in the lowest absorption range [23]. The slope of Fig. 4 yields the reciprocal of the E_e value. The compositional dependence of the both E_g and E_e values were shown in Fig. 5. From this figure it was observed that, the E_g is indirectly proportional to the Ee values which satisfy Mott and Davies model. In accordance with this model as the width of band gap increases the Urbach energy decreases. The later dependence on the disorder and defects degree in the amorphous matrix. Thus, the decrease in E_e values leads to increasing the E_g and $\sqrt{\beta}$ values. Furthermore, the observed results can be interpreted in terms of the chemical bond approach [24]. This model may be satisfied for As-Se-S glasses. Depending on the bond energy (De), the relative probability of its formation was investigated through the probability function

$e^{De/Kt}$ [25]. Se-S (2.05 eV), As-Se (1.81 eV) behind excess of Se-Se (1.91 eV) have a significant probability of formation for glassy samples with ($0.0 \leq S \leq 20\ at.\%$.

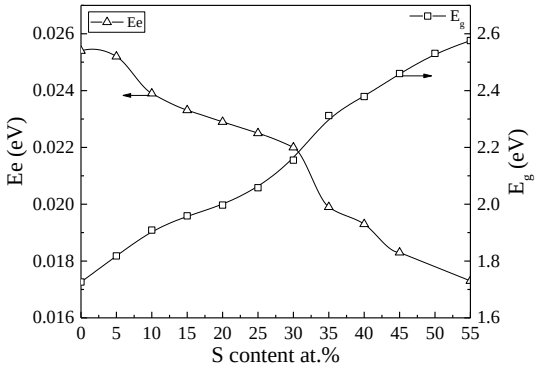

Fig. 5. Compositional dependence E_g and E_e values for $As_{0.20}Se_{0.80-x}S_x$ films.

Although As-S energy bond (1.95 eV) is higher that of As-Se but it can't be formed due the S amount isn't enough to saturate all Se valances leading to the formation of As-Se bonds. With increasing S content up to 25 at.% We reach the stoichiometry composition ($As_{0.20}Se_{0.55}S_{0.25}$). Here only Se-S and As-Se bonds are found and Se-Se bonds disappeared. Any further addition of S (from 30 t0 40 at.%) content the homopolar As-As (1.39 eV) bonds are gradually formed at the expense of Se-S and As-Se bonds. The As-Se bonds are disappeared at 35 at.% S content. With increasing S content (>40 at.%) the S amount became enough to form As-S at the expense of As-As bonds which disappear at 55 at.% S content. At this concentration we arrive at stoichiometric composition ($As_{0.20}Se_{0.25}S_{0.55}$) with only Se-S and As-S bonds. Knowing the formed bond energy in each glass composition, the cohesive energy (Ce) can be estimated through the summation of the expected bond energies in the glassy system. The estimated cohesive energies were listed in Table 1. It was found the Ce values increases with increasing S content up to 25 at.% which is consistent with the observed increase in E_g values. Further addition of S content the weakness As-As bonds will be appear and Ce decreases up to 45 at.% S content. Hear the Ce values return to increases due to the formation of strongest As-S bonds.

Table 1. Distribution of the chemical bonds and cohesive energy of As-Se-S glasses.

S at.%	Distribution of the chemical bonds					CE (eV)	$\frac{\sqrt{\beta}}{\sqrt{cm^{-1}.eV}}$
	As-Se	Se-Se	Se-S	As- S	As-As		
0	0.5455	0.4545	--	--	--	2.04	707
5	0.5455	0.3636	0.0909	--	--	2.05	715
10	0.5455	0.2727	0.1818	--	--	2.07	723
15	0.5455	0.1818	0.2727	--	--	2.08	735
20	0.5455	0.0909	0.3636	--	--	2.09	746
25	0.5455	--	0.4545	--	--	2.11	753
30	0.3636	--	0.5455	--	0.0909	2.09	761
35	0.1818	--	0.6364	--	0.1818	2.07	770
40	--	--	0.7273	--	0.2727	2.05	782
45	--	--	0.6364	0.1818	0.1818	2.10	795
50	--	--	0.5455	0.3636	0.0909	2.15	806
55	--	--	0.4545	0.5455	0	2.20	817

4. Conclusions

Different compositions of $As_{0.20}Se_{0.80-x}S_x$ $(0.0 \leq x \leq 0.55\ at.\%)$ glasses were prepared in the bulk and thin films. The glass density, molar volume as well as compactness were measured. The absorption coefficient was estimated based on the measured film absorptance. The

glass density, compactness, the Tauc parameter $\sqrt{\beta}$ and the Urbach energy are decrease with the addition of S amount whereas the molar volume and the optical gap are increases. The obtained results are consistent with each others and well discussed in terms of the chemical bonds and the Mott and Davis model.

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