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Synthesis and theoretical characterization of ternary $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses

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ABSTRACT

The $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \leq x \leq 12$ at.%) chalcogenide alloys have been synthesized by the conventional melt quenching technique. The physical properties such as the mean coordination number, density, molar volume, compactness, overall bond energy, and cohesive energy were estimated for the Cu doped Ge-Se glassy alloys. The chemical bond approach (CBA) was used to predict the type and proportion of the formed bonds in the studied glasses. Subsequently, several structural and physical properties have been estimated. The results show that the studied glasses are rigidly connected, having an average coordination number increase from 2.6 to 2.77. The density and glass compactness show an increase with the Cu content, whereas the main atomic volume decreases. The cohesive energy and the heat of atomization show a similar behavior trend with the enhancement of Cu % in the Ge-Se binary glasses. The optical band gap was estimated theoretically compared with the previously published experimental values for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \leq x \leq 12$ at.%) thin films. The covalency parameter >91% for the studied glasses so that the compositions may be used as a stable glass former. Furthermore, the mechanical properties as the elastic bulk modulus, Poisson's ratio, Young's modulus, micro-hardness, and Debye temperature were investigated as a function of the Cu content.

Introduction

The chalcogenide glasses based on chalcogen elements like sulfur, selenium, and tellurium in the multicomponent system are promising materials in various applications like thermal imaging, optical storage, xerography, optical fibers, and biosensing, etc. Chalcogenide glasses are seeking more interest in the field of modern science and technology since their physical properties are interesting [1–4]. These glasses transparency is extended from the mid to far-infrared region [5,6]. Furthermore, these glasses exhibit low phonon energy, high refractive index, and wide transmission range [7,8].

Although Se has disadvantages such as a short lifetime and low sensitivity, it has high glass-forming ability, so it represents a suitable host matrix for investigating chalcogenide glasses in the bulk and thin film forms [9–11]. Ge has been chosen to minimize the drawbacks of pure Se where the Ge-Se-based glasses have good physical, optical, mechanical, electrical, and thermoelectric properties [12–18]. In this study, Cu is selected due to its attractive and essential applications as a third element in the Ge-Se framework. The addition of Cu improves several physicochemical, optical, and thermal properties of the glasses [19–21]. The Cu-containing chalcogenide glasses are very significant owing to their applications in the phase change erasable memory devices, and they possess a single glass transition temperature [22,23]. For the rewritable disks, the single crystallization temperature is the essential condition which different Cu doped chalcogenide glasses can obtain.

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The compositional dependence of the optical properties such as absorption coefficient, extinction coefficient, energy gap, refractive index, single oscillator energy, dispersion energy, Urbach energy, dielectric constants, optical conductivity, dissipation factor, as well as the positions of the valence and conduction bands edges for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \le x \le 12$ at.%) system was reported [24]. It was revealed that the energy gap decreased from 2.21 to 1.86 eV when the Cu content increased from 0 to 12 at.%. Using the CBA, the type and proportion of the bonds that occur in chalcogenide glasses have been obtained [25–30]. Then many physical parameters were estimated. Furthermore, the theoretical prediction of the energy gap using the chemical bond distribution has been estimated.

The present study's main aim is to investigate the influence of Cu addition into the $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \le x \le 12$ at.%) system on the physical parameters like mean coordination number, density, molar volume, compactness etc. The cohesive energy has been discussed using the chemical bond approach (CBA) over the varied compositions. In addition to this, the mechanical properties such as the elastic bulk modulus, Poisson's ratio, Young's modulus, micro-hardness, and Debye temperature were also investigated with the enhancement of Cu content in the base composition.

Experimental details

The bulk samples of the ternary $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \le x \le 12$ at.%) system have been prepared by the conventional melt quenching technique. The materials of 5 N purity have been weighed by electric balance by their amount of atomic weight and put in quartz ampoules. After that, the ampoules were sealed under a vacuum (10^{-4} Torr). The sealed ampoules were kept in the muffle furnace at 1273 K for 24 h to maintain the melt's homogeneity. The synthesis information, elemental compositions, and the amorphous nature of the synthesized specimens were discussed in our previous paper [24]. The glass density, ρ, was experimentally determined using the immersion method as detailed in references [31,32]. The glass mean atomic volume was estimated with the help of ρ then the glass compactness, δ, was estimated. The error in calculating the density then in molar volume and compactness was measured to be less than 1%. The longitudinal (v_L) and shear (v_T) ultrasonic velocities were recorded at 300 K via the pulse-echo technique. According to this technique, x-cut and y-cut transducers (KARL DEUTSCH) conducted at a basic frequency 4 MHz in conjunction with an ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085). The uncertainty in v_L and v_T is ± 10 m/s.

Results and discussion

The chemical bond approach (CBA) predicts the type and proportion of the formed bonds in chalcogenide glasses. Subsequently, several structural and physical properties, such as the cohesive energy (*CE*), the mean bond energy ($\langle E \rangle$), the overall electronegativity difference ($\Delta\chi$), the degree of ionicity (*Ion*), and the degree of covalency (Cov) can be estimated.

The glass density (ρ), molar volume (V_m), and compactness (δ) are important factors used to characterize the glass. The density of the bulk $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \le x \le 12$ at.%) glasses was measured using the Archimedes technique. Knowing the sample weight in the air (W_{air}) and the toluene (W_{tol}), ρ of the studied glasses can be obtained from the equation [31,32]:

$$\rho = \frac{W_{air}}{W_{air} - W_{tol}}\rho_{tol} \tag{1}$$

where ρ_{tol} is the density of toluene. V_m of the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses was estimated using the relation [32]:

$$V_m = \rho^{-1}\sum_i c_i A_i \tag{2}$$

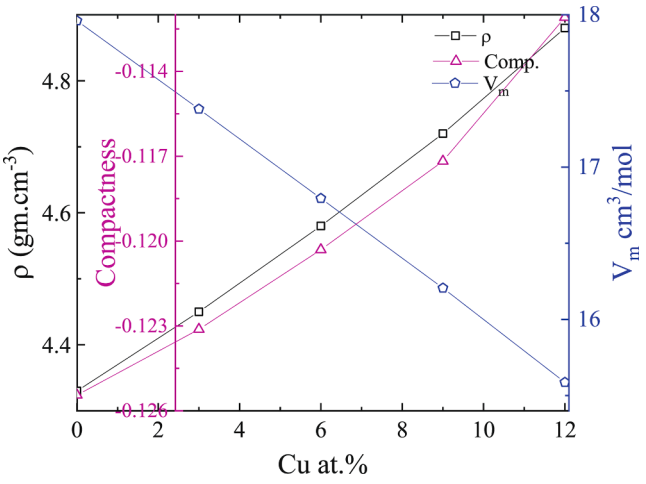

Fig. 1. The compositional dependence of ρ, V_m, and δ of the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

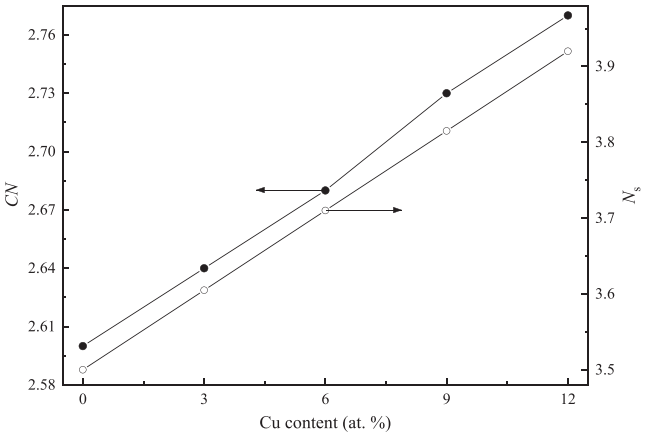

Fig. 2. Variations of *CN* and *Ns* versus Cu content for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

where c_i and A_i represent the atomic fraction and atomic weight of the i^{th} element.

δ was estimated by the formula [33–35]:

$$\delta = \frac{\sum_i c_i A_i \rho_i^{-1}}{\sum_i c_i A_i \rho^{-1}} - 1 \tag{3}$$

where ρ_i is the density of i^{th} element. The density and glass compactness show an increase with the Cu content, whereas the main atomic volume decreases (see Fig. 1).

The glass constraints theory proposed by Phillips and Thorpe [36,37] stated that the rigidity of glass might be inferred by knowing the coordination number (*CN*). The *CN* of the constituent elements (Ge, Se, and Cu) given in ref. [38] was used to estimate the CN of the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses:

$$CN = \sum x_i \cdot CN_i \tag{4}$$

where x_i is the mole fraction, and CN_i is the coordination number of the i^{th} element. The constraints number (*Ns*) is connected to the rigidity of the glass network. It is calculated using the values of *CN* via the relation [39]:

$$N_s = CN/2 + (2CN - 3) \tag{5}$$

The values of *CN* and N_s have been calculated for the

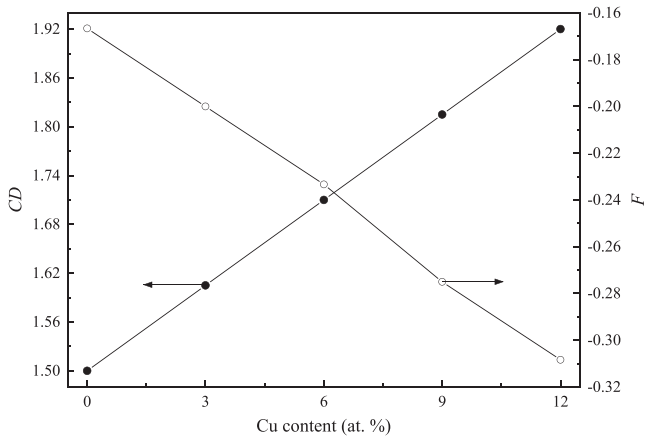

Fig. 3. Variations of CD and F versus Cu content for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

$Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses and presented in Fig. 2. This figure shows that both *CN* and N_s increase by increasing the Cu content. This increase is associated with an increase of the network cross-linking, which can be ascribed to the incorporation of the 4-fold Cu atoms [40]. The increase in *CN* as well as N_s reflects the increase in the rigidity of the network by increasing the Cu content. The $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses are rigidly connected, where $CN > 2.4$. This value (2.4) represents the rigidity's percolation threshold as supposed by the constraints theory [36,37].

Based on the concept of *CN* proposed by Philips [41], Thorpe [42] supposed that the glass network consists of a mixture of rigid and floppy regions. The glass network transforms from a floppy structure to a rigid structure at the rigidity percolation threshold ($CN = 2.4$) [43]. Thorpe correlated the floppy modes with the *CN* by the following equation [42]:

$$F = 2 - \frac{5}{6}CN \tag{6}$$

The constraints number (*Ns*) can be used to evaluate the crosslinking density (*CD*). *Ns* and *CD* reflect the glass rigidity. Values of *CD* were estimated for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses according to the equation [44]:

$$CD = N_s - 2 \tag{7}$$

The compositional dependence of the estimated values of *F* and *CD* was presented in Fig. 3. As can be seen, the floppy modes' values decrease, whereas the crosslinking density increases by increasing the Cu content. This behavior shows that the addition of Cu increases the glass rigidity. The negative values of *F* indicate that the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses are rigid glasses. This agrees with the results previously discussed concerning the increase of *CN* and N_s with an increase of Cu content.

The rigidity of the glass network may be predicted by getting the overall mean bond energy ($\langle E \rangle$). To estimate $\langle E \rangle$ for the studied glasses, the deviation of stoichiometry (*r*) is needed with the chemical bonds' distribution. Values of *r* for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \le x \le 12$ at.%) glasses was estimated as the ratio of chalcogen to non-chalcogen proportions using the following equation [45,46]:

$$r = \frac{x_{Se}.CN_{Se}}{x_{Ge}.CN_{Ge} + x_{Cu}.CN_{Cu}} \tag{8}$$

where x_{Se}, x_{Ge}, and x_{Cu} are the mole fractions of Se, Ge and Cu, respectively. According to the *r* values (see Table 1), the first two compositions (x = 0 and 3 at.%) represent chalcogen-rich glasses ($r > 1$), whereas the others represent the chalcogen-poor where *r* is less than 1. The overall mean bond energy $\langle E \rangle$ for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses was estimated. A detailed procedure for estimating $\langle E \rangle$ can be found in previous papers [47,48]. The obtained values of $\langle E \rangle$ are listed in Table 1. As shown in the table, $\langle E \rangle$ increases with an increase of the Cu content, which reflects the increase of the glasses' rigidity with the addition of Cu.

Other important parameters for characterizing the studied glasses are the cohesive energy (*CE*), and the average heat of atomization (H_s). Values of *CE* were determined by summing the bond energies [38]:

$$CE = \sum_i C_i \cdot BE_i / 100 \tag{9}$$

C_i and BE_i represent the number and the energy of the i^{th} bond. The estimated values of the *CE* for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses are shown in Fig. 4. One can notice that *CE* increases with an increase in the Cu content. The increase of the *CE* may be attributed to an increase of the strongest Cu-Se bonds (62.42 kcal/mol) with increasing the Cu concentration.

The heat of atomization (H_s) of the glasses may be estimated according to the following equation:

$$H_S = \sum x_i \cdot H_s^i \tag{10}$$

where x_i is the mole fraction, and H_s^i is the heat of atomization of the i^{th} element. Using the H_s values of the constituent elements (Ge, Se, and Cu) given in ref. [38], the values of H_s for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses were estimated and shown in Fig. 4. One can notice from this figure that,

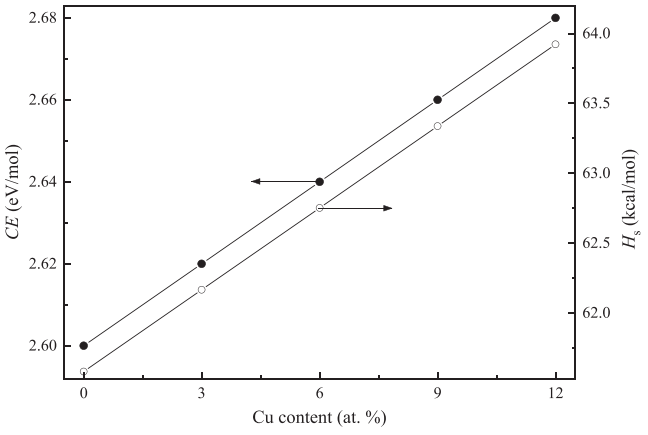

Fig. 4. Plots of *CE* and H_s for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

Table 1
Some of the physical and mechanical properties $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

x at.%	LP	*r*	$\langle E \rangle$	E_g [24]	v_L	v_T	C_{11}	C_{44}	*K*	σ	Y	H	θ_D
			eV		m/s		GNm^{-2}				GNm^{-2}		K
0.0[49]	–	–	–	–	–	–	–	–	12.64	0.264	17.90	–	–
0.0	2.80	1.17	2.71	2.21	2256	1279	22.04	7.08	2.59	0.263	17.89	1.12	136.68
3.0	2.63	1.03	2.85	2.12	2350	1330	24.58	7.87	14.08	0.264	19.91	1.24	143.72
6.0	2.45	0.92	2.96	2.01	2420	1390	26.82	8.85	5.02	.254	22.19	1.45	151.74
9.0	2.28	0.82	3.02	1.92	2504	1460	29.59	10.06	16.18	0.242	25.00	1.73	161.07
12.0	2.10	0.72	3.06	1.86	2590	1534	32.74	11.48	17.42		28.25	2.07	171.20

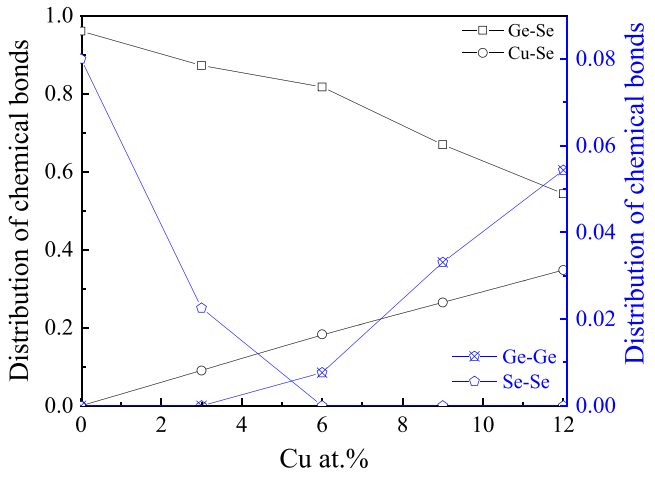

Fig. 5. The expected chemical bonds distribution for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

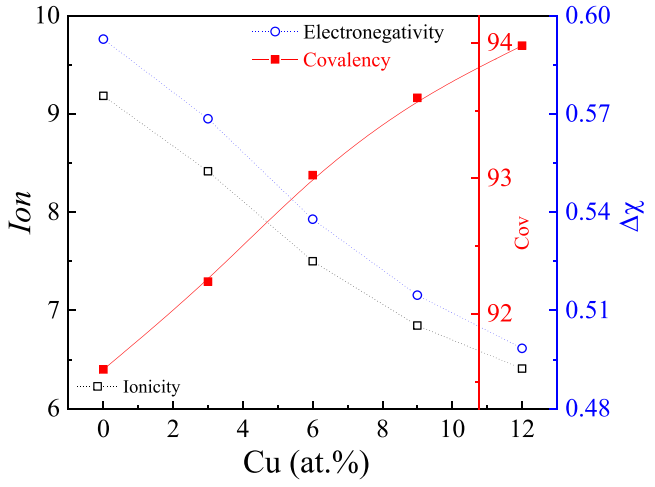

Fig. 6. Plots of Δχ, *Ion* and Cov versus Cu content for $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses.

H_s of the studied glasses increases with increasing the Cu content. This increase may be due to the addition of Cu atoms with a high value of H_s (81.1 kcal/mol).

The bandgap should be estimated to get the correlation between the optical and physicochemical properties for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses. The bond distribution may be used to get the bandgap of the studied glasses theoretically. Using the bond energies and electronegativities of the constituent elements (Ge, Se, and Cu) given in ref. [38] the formed heteropolar bonds of the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses were estimated. The expected formed bonds, according to the chemical bond approach, in the studied glasses are Cu-Se ($D_{Cu\text{-}Se}$ = 62.42 kcal/mol), Ge-Se ($D_{Ge\text{-}Se}$ = 49.44 kcal/mol), Se-Se ($D_{Se\text{-}Se}$ = 44.04 kcal/mol), and Ge-Ge ($D_{Ge\text{-}Ge}$ = 37.6 kcal/mol). The proportions of the formed bonds are shown in Fig. 5.

Since the glass network is considered a giant macromolecule, we could calculate its overall electronegativity to estimate the degree of iconicity or covalency of the whole compound. In fact, ionicity or electronegativity is very important to estimate how much electrons are itinerant as well as the degree of stretching and/or bending of chemical bonds. This idea was introduced first by Pauling [50] for single chemical bonds in molecules and used by Philips [51] in crystalline structures. The overall electronegativity difference could be estimated from the hetero-polar bonds electronegativity difference weighted by the proportion of each present bond as following:

$$\Delta\chi = P_{A-B}\cdot|\chi_A - \chi_B| + P_{B-C}\cdot|\chi_B - \chi_C| + P_{A-C}\cdot|\chi_A - \chi_C| \quad (11)$$

As the glass's physical properties are correlated to the formed bonds, it is useful to calculate the degree of ionicity (*Ion*) of the glasses. According to Pauling [50], *Ion* can be calculated using the relation:

$$Ion = 100\left(1 - exp\left[-\frac{\Delta\chi^2}{4}\right]\right) \quad (12)$$

Fig. 6 illustrates the estimated Δχ, *Ion* and *Cov* as a function of Cu content for $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses. One can notice from the figure that both Δχ Moreover, *Ion* decrease whereas *Cov* increases with increasing the Cu content. This behavior may be due to the increase in the glass covalency ($Cov = 100.exp(-\Delta\chi^2/4)$). Thus, the iconicity declines as well as Δχ. Cu is more electropositive (electronegativity χ_{cu} = 1.9) than Ge (χ_{Ge} = 2.01) and Se (χ_{Se} = 2.55). So increasing the Cu content decreases the electronegativity of the glasses and hence decreases the degree of ionicity.

The two velocities v_L and v_T, with the density, have been used to estimate the two independent second-order elastic constants, C_{11} and C_{44}. In the case of absolute longitudinal waves $C_{11} = \rho v_L^2$ and in the case of absolute transverse waves $C_{44} = \rho v_T^2$. Then one can estimate: the elastic bulk modulus (*K*) [52,53]:

$$K = C_{11} - 1.33C_{44}, \quad (13)$$

Poisson's ratio (θ)

$$\epsilon = (C_{11} - 2C_{44})(2C_{11} - 2C_{44})^{-1}, \quad (14)$$

Young's modulus (*Y*):

$$Y = 2C_{44}(1 + \epsilon) \quad (15)$$

Micro-hardness (H):

$$H = (1 - 2\epsilon)Y/(6(1 + \epsilon)) \quad (16)$$

The Debye temperature (θ_D)

$$\theta_D = h\nu_m/k_b\sqrt[3]{3nN/4\pi v_M} \quad (17)$$

where *h*, k_b, and *N* with the same physical meaning, n is the atoms number and ν_m is the average speed of sound ($\nu_m = \sqrt[-3]{v_L^{-3} + 2v_T^{-3}}$). The uncertainty in the measurement of the elastic moduli is ±0.15 GPa.

The longitudinal (v_L) and shear (v_T) ultrasonic velocities of the glassy system with different at.% of Cu content are depicted in Table 1. The ultrasonic velocities increased with the increase of copper concentration, and the values of v_L are higher than that of v_T. The changes in glass structure depend on the propagation of both longitudinal and shear wave velocities in the bulk samples [52,53]. It was known that the Cu additions to GeSe glasses lead to the formation of the strongest Cu-Se bonds (62.42 kcal/mol) at the expense of Ge–Se bonds (49.44 kcal/mol). The distribution of the expected chemical bond was shown in Fig. 5. As a result, both velocities (v_L) and (v_T) were increased. The increase in v_L *and* v_T reflects the observed increase in the elastic moduli and Debye temperature. In other words, the cu additions increase the glass density and compactness, which reflect the increase of glass rigidity. Simultaneously, the molar volume decreases, which confirmed the formation of strong bonds with short lengths [54–56]. Such bonds are the main reason for increasing the cohesive energy and average heats of atomization as well as the enhancement of elastic moduli.

The theoretical bandgap $E_g^{(th)}$ of the system could be estimated using the chemical bond distribution from the equation [27]:

$$E_g^{(th)} = \sum P_i \cdot E_g(D_i) \quad (18)$$

P_i and $E_g(D_i)$ represent the proportion and energy gap of the i^{th} bond, respectively. This estimation takes into account the local surrounding of

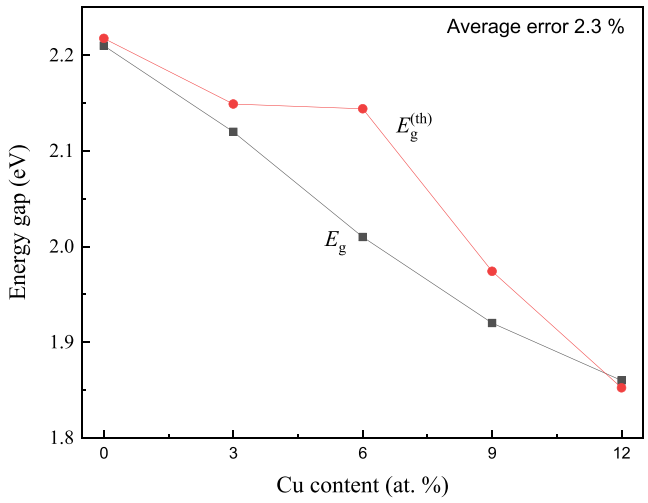

Fig. 7. Experimental and theoretical estimations of the band gaps versus the composition for $Cu_x(Ge_{30}Se_{70})_{100-x}$ thin films.

every atom, as stated by the CBA. The compositional dependence of the estimated $E_g^{(th)}$ Furthermore, the experimental band gap (E_g obtained from the previously published paper [24]) for the $Cu_x(Ge_{30}Se_{70})_{100-x}$ system are shown in Fig. 7.

As shown in this figure both the $E_g^{(th)}$ and E_g decrease with an increase of Cu content. Values of $E_g^{(th)}$ and E_g are in good agreement with each other, with an average error of about 2.3%.

Conclusion

The effect of composition on the physical parameters of $Cu_x(Ge_{30}Se_{70})_{100-x}$ ($0 \leq x \leq 12$ at.%) system has been theoretically investigated. The average coordination number (*CN*), the total number of interatomic force field constraints per atom (N_s), the crosslink density (*CD*), cohesive energy (*CE*), and the average heat of atomization (*Hs*) increases with the enhancement of Cu in the $Cu_x(Ge_{30}Se_{70})_{100-x}$ glasses. The density (ρ) and compactness (δ) of the system increases, whereas the mean atomic volume (V_m) decreases with the enhancement of Cu amounts in the present glassy system. The increase of *CE*, *Hs* and ρ reflects the increase of the elastic moduli, Posaon's ratio and Deby's temperature. The optical gap decreased from 2.21 eV for $Ge_{30}S_{70}$ to 1.86 eV for $Cu_{12}(Ge_{30}Se_{70})_{88}$ films, i.e. the wavelengths corresponding to E_g values lie in the visible range of spectra, which make these films candidates for the solar cell application. In the present investigated samples, the covalence parameter is >91% so that the system may be used in infrared applications.

CRediT authorship contribution statement

H.I. El Saeedy: Conceptualization, Funding acquisition, Writing - original draft. **H.A. Yakout:** Conceptualization, Methodology, Writing - original draft, Investigation. **K.A. Aly:** Writing - original draft, Investigation, Conceptualization. **Y.B. Saddeek:** Conceptualization, Investigation, Methodology, Writing - review & editing, Supervision. **A. Dahshan:** Investigation, Writing - original draft, Writing - review & editing, Supervision. **H.A.A. Sidek:** Investigation, Conceptualization, Writing - review & editing, Supervision. **K.A. Matori:** Investigation, Conceptualization, Writing - review & editing, Supervision. **M.H.M. Zaid:** Investigation, Conceptualization, Writing - review & editing, Supervision. **Hesham M.H. Zakaly:** Writing - original draft, Investigation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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