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 ≤ x ≤ 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 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 ≤ x ≤ 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 transition 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 ≤ x ≤ 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 ≤ x ≤ 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 ≤ x ≤ 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 ($\rho$), 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 and shear (ν) 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 ν$$_x$$ and ν$$_S$$ 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 (E'), the overall electronegativity difference ($\Delta\chi$), the degree of ionicity (ion), and the degree of covalency (Cov) can be estimated.

The glass density ($\rho$), ρ, molar volume ($V_m$), and compactness ($\delta$) are important factors used to characterize the glass. The density of the bulk Cu$_x$(Ge$_{30}$Se$_{70}$)$_{100-x}$ (0 ≤ x ≤ 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]:

$$\rho = \frac{W_{air}}{W_{tol} - W_{air}}$$  \hspace{1cm} (1)

where $\rho_{tol}$ is the density of toluene. $V_m$ of the Cu$_x$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses was estimated using the relation [32]:

$$V_m = \rho^{-1} \sum_i c_i A_i$$  \hspace{1cm} (2)

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

$\delta$ was estimated by the formula [33–35]:

$$\delta = \sum_i c_i A_i \rho_i^{-1} - 1$$  \hspace{1cm} (3)

where $\rho_i$ 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:

$$CN = \sum x_iCN_i$$  \hspace{1cm} (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]:

$$N_s = CN/2 + (2CN - 3)$$  \hspace{1cm} (5)

The values of CN and Ns have been calculated for the
Cu$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses and presented in Fig. 2. This figure shows that both CN and $N_i$ 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 $N_i$ reflects the increase in the rigidity of the network by increasing the Cu content. The Cu$_4$(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]:

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

(6)

The constraints number ($N_s$) can be used to evaluate the crosslinking density (CD). $N_s$ and CD reflect the glass rigidity. Values of CD were estimated for the Cu$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses according to the equation [44]:

$$ CD = N_s - 2 $$

(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$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses are rigid glasses. This agrees with the results previously discussed concerning the increase of $CN$ and $N_i$ with an increase of Cu content.

The rigidity of the glass network may be predicted by getting the overall mean bond energy ($E$). To estimate ($E$) for the studied glasses, the deviation of stoichiometry ($r$) is needed with the chemical bonds' distribution. Values of $r$ for the Cu$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ ($0 \leq x \leq 12$ at.%) glasses was estimated as the ratio of chalcogen to non-chalcogen proportions using the following equation [45,46]:

$$ r = \frac{x_{Ga}, CN_{Ga}}{x_{Ga}, CN_{Ga} + x_{Cu}, CN_{Cu}} $$

(8)

where $x_{Ga}$, $x_{Ge}$, 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 ($E$) for the Cu$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses was estimated. A detailed procedure for estimating ($E$) can be found in previous papers [47,48]. The obtained values of ($E$) are listed in Table 1. As shown in the table, ($E$) 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]:

$$ CE = \sum_i C_i BE_i/100 $$

(9)

$C_i$ and $BE_i$ represent the number and the energy of the $i^{th}$ bond. The estimated values of CE for the Cu$_4$(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:

$$ H_s = \sum_i x_i H_{i}^r $$

(10)

where $x_i$ is the mole fraction, and $H_{i}^r$ 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$_4$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses were estimated and shown in Fig. 4. One can notice from this figure that,

\[ \text{Table 1} \]

| x at.% | $\text{LP}$ | $r$ | $|E|$ | $E$ [24] | $v_1$ | $v_2$ | $C_{11}$ | $C_{44}$ | $K$ | $r$ | $Y$ | $H$ | $\delta_a$ |
|--------|-------------|-----|------|--------|-------|-------|----------|----------|----|-----|-----|-----|----------|
| 0.0 [49] | - | - | - | - | 2.71 | 2.21 | 2256 | 1279 | 22.04 | 7.08 | 2.59 | 0.264 | 17.90 | - | - |
| 0.0 | 2.80 | 1.17 | - | - | - | - | 2256 | 1279 | 22.04 | 7.08 | 2.59 | 0.264 | 17.90 | - | - |
| 3.0 | 2.63 | 1.03 | 2.85 | 2.12 | 2250 | 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 | 28.82 | 8.85 | 15.02 | 0.254 | 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 | 0.225 | 28.25 | 2.07 | 171.20 |

\[ \text{Fig. 3. Variations of CD and F versus Cu content for the Cu}_4(\text{Ge}_{30}\text{Se}_{70})_{100-x} \text{ glasses.} \]

\[ \text{Fig. 4. Plots of CE and } H_s \text{ for the Cu}_4(\text{Ge}_{30}\text{Se}_{70})_{100-x} \text{ glasses.} \]
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Fig. 5. The expected chemical bonds distribution for the Cu70(Ge30Se70)100-x glasses.

Fig. 6. Plots of $\Delta \chi$, Ion and Cov versus Cu content for Cu70(Ge30Se70)100-x glasses.

$H_i$ 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 $H_i$ (81.1 kcal/mol).

The bandgap should be estimated to get the correlation between the optical and physicochemical properties for the Cu70(Ge30Se70)100-x glasses. The bond distribution may be used to get the bandgap of the studied glasses theoretically. Using the bond energies and electronegativity of the constituent elements (Ge, Se, and Cu) given in ref. [38] the formed heteropolar bonds of the Cu70(Ge30Se70)100-x glasses were estimated. The expected formed bonds, according to the chemical bond approach, in the studied glasses are Cu-Se (D_{Cu-Se} = 62.42 kcal/mol), Ge-Se (D_{Ge-Se} = 49.44 kcal/mol), Se-Se (D_{Se-Se} = 44.04 kcal/mol), and Ge-Ge (D_{Ge-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, iconicity or covalency could calculate its overall electronegativity to estimate the degree of ionicity or electronegativity difference weighted by the number and proportion of each bond present as following:

$$\Delta \chi = P_{a-b} |\chi_a - \chi_b| + P_{b-c} |\chi_b - \chi_c| + P_{c-a} |\chi_{-c} - \chi_{-a}|$$

(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:

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

(12)

Fig. 6 illustrates the estimated $\Delta \chi$, Ion and Cov as a function of Cu content for Cu70(Ge30Se70)100-x glasses. One can notice from the figure that both $\Delta \chi$ Moreover, Ion decrease whereas Cov increases with increasing the Cu content. This behavior may be due to the increase in the glass covalency (Cov = 100.0.exp(−Δ$\chi^2$/4)). Thus, the iconicity declines as well as $\Delta \chi$. The Cu is more electropositive (electronegativity $\chi_{\text{Cu}}$ = 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]:

$$K = C_{11} - 1.33C_{44}.$$  

(13)

Poisson’s ratio ($\nu$):

$$\nu = (C_{11} - 2C_{44})/(2C_{11} - 2C_{44})^{-1},$$

(14)

Young’s modulus ($Y$):

$$Y = 2C_{44}(1 + \nu),$$

(15)

Micro-hardness (H):

$$H = (1 - 2\nu)Y/(6(1 + \nu)),$$

(16)

The Debye temperature ($\theta_D$):

$$\theta_D = h\nu_m/\sqrt{3N\pi/4\pi^2},$$

(17)

where $h$, $k_B$, and $N$ with the same physical meaning, $n$ is the atoms number and $v_m$ is the average speed of sound ($v_m = \sqrt{\frac{1}{2}v_l^3 + 2v_T^3}$). 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 $E_b^{th}$ of the system could be estimated using the chemical bond distribution from the equation [27]:

$$E_b^{th} = \sum P_i E_i(D_i)$$

(18)

$P_i$ and $E_i(D_i)$ represent the proportion and energy gap of the $i^{th}$ bond, respectively. This estimation takes into account the local surrounding of
every atom, as stated by the CBA. The compositional dependence of the estimated $E_g^{(h)}$. Furthermore, the experimental band gap ($E_g$ obtained from the previously published paper [24]) for the Cu$_x$(Ge$_{20}$Se$_{70}$)$_{100-x}$ system are shown in Fig. 7.

As shown in this figure both the $E_g^{(h)}$ and $E_g$ decrease with an increase of Cu content. Values of $E_g^{(h)}$ 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$_{20}$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 ($N_c$), the crosslink density (CD), cohesive energy ($CE$), and the average heat of atomization ($H_a$) increases with the enhancement of Cu in the Cu$_x$(Ge$_{20}$Se$_{70}$)$_{100-x}$ glasses. The density ($\rho$) and compactness ($\delta$) 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 $CE$, $H_a$ and $\rho$ reflects the increase of the elastic moduli, Poisson’s ratio and Deby’s temperature. The optical gap decreased from 2.21 eV for Ge$_{20}$Se$_{70}$ to 1.86 eV for Cu$_x$(Ge$_{20}$Se$_{70}$)$_{100-x}$ 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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Fig. 7. Experimental and theoretical estimations of the band gaps versus the composition for Cu$_x$(Ge$_{20}$Se$_{70}$)$_{100-x}$ thin films.
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