Synthesis and theoretical characterization of ternary Cu$_x$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses

H.I. El Saeedy$^a$, H.A. Yakout$^a$, K.A. Aly$^{b,c}$, Y.B. Saddeek$^{b,d}$, A. Dahshan$^{a,e}$, H.A.A. Sidek$^f$, K. A. Matori$^g$, M.H.M. Zaid$^f$, H.M.H. Zakaly$^{b,s}$

$^a$ Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia
$^b$ Department of Physics, Faculty of Science, Al-Azhar University, 71524 Assiu, Egypt
$^c$ University of Jeddah, College of Science and Arts at Khuls, Department of Physics, Jeddah, Saudi Arabia
$^d$ Physics Department, Collage of Science in Zulfi, Majmaah University, 11952, Saudi Arabia
$^e$ Department of Physics, Faculty of Science, Port Said University, Port Said, Egypt
$^f$ Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
$^g$ Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russia

**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 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 ≤ 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.

**Keywords:**
Chalcogenide glasses
Chemical bond approach
Physical properties
Mechanical properties

**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 due 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.

$^*$ Corresponding authors at: Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russia (H.M.H. Zakaly); Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia (M.H.M. Zaid).

E-mail addresses: mhmzaid@upm.edu.my (M.H.M. Zaid), h.m.zakaly@azhar.edu.eg, h.m.zakaly@gmail.com (H.M.H. Zakaly).

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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 \( \text{Cu}_x(\text{Ge}_{30}\text{Se}_{70})_{100-x} \) \((0 \leq x \leq 12 \text{ at.}%)\) 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 revealed that the energy gap decreased from 2.21 to 1.86 eV when the Cu content increased from 0 to 12 at.%. The present study’s main aim is to investigate the influence of Cu addition into the \( \text{Cu}_x(\text{Ge}_{30}\text{Se}_{70})_{100-x} \) \((0 \leq x \leq 12 \text{ at.}%)\) 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 \( \text{Cu}_x(\text{Ge}_{30}\text{Se}_{70})_{100-x} \) \((0 \leq x \leq 12 \text{ at.}%)\) 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 \((10^{-4} \text{ Torr})\). 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, \( \rho \), was experimentally determined using the immersion method as detailed in references \([31,32]\). The glass mean atomic volume was estimated with the help of \( \rho \) then the glass compactness, \( \delta \), 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 \( \pm 10 \text{ m/s} \).

### 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 (\( \langle E_i \rangle \)), the overall electronegativity difference (\( \Delta \chi \)), the degree of ionicity (\( \chi \)), and the degree of covalency (\( \text{Cov} \)) can be estimated.

The glass density (\( \rho \)), molar volume (\( V_m \)), and compactness (\( \delta \)) are important factors used to characterize the glass. The density of the bulk \( \text{Cu}_x(\text{Ge}_{30}\text{Se}_{70})_{100-x} \) \((0 \leq x \leq 12 \text{ at.}%)\) glasses was measured using the Archimedes technique. Knowing the sample weight in the air (\( W_{\text{air}} \)) and the toluene (\( W_{\text{tol}} \), \( \rho \) of the studied glasses can be obtained from the equation \([31,32]\):

\[
\rho = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{tol}}}\rho_{\text{tol}} \tag{1}
\]

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

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

where \( c_i \) and \( A_i \) represent the atomic fraction and atomic weight of the \( i^{th} \) element. \( \delta \) was estimated by the formula \([33-35]\):

\[
\delta = \frac{\sum_i c_i A_i \rho_i^{-1}}{\sum_i c_i A_i} - 1 \tag{3}
\]

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 \( \text{Cu}_x(\text{Ge}_{30}\text{Se}_{70})_{100-x} \) 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 (\( N_i \)) is connected to the rigidity of the glass network. It is calculated using the values of \( CN \) via the relation \([39]\):

\[
N_i = CN/2 + (2CN - 3) \tag{5}
\]

The values of \( CN \) and \( N_i \) have been calculated for the
Cu$_3$(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$_3$(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$_3$(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$_3$(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$_3$(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]:

$$r = \frac{x_{Ge}C_{Ge} + x_{Cu}C_{Cu}}{x_{Ge}C_{Ge}}$$

(8)

where $x_{Ge}$, $x_{Cu}$, 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$_3$(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]:

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

(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$_3$(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:

$$H_s = \sum x_i\cdot H_i$$

(10)

where $x_i$ is the mole fraction, and $H_i$ 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$_3$(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$_3$(Ge$_{30}$Se$_{70}$)$_{100-x}$ glasses.](image-url)

Table 1

<table>
<thead>
<tr>
<th>at.%</th>
<th>LP</th>
<th>$r$</th>
<th>$E$ eV</th>
<th>$E_b$ [24]</th>
<th>$v_i$ m/s</th>
<th>$v_f$ m/s</th>
<th>$C_{11}$ GNm$^{-2}$</th>
<th>$C_{44}$ GNm$^{-2}$</th>
<th>$K$</th>
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<th>$Y$</th>
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<th>$\theta_s$ K</th>
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<td>2.71</td>
<td>2.21</td>
<td>2256</td>
<td>1279</td>
<td>22.04</td>
<td>7.08</td>
<td>2.59</td>
<td>0.264</td>
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<td>2.85</td>
<td>2.12</td>
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<td>1330</td>
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<td>2.01</td>
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<td>1390</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.72</td>
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<td>1.86</td>
<td>2590</td>
<td>1534</td>
<td>32.74</td>
<td>11.48</td>
<td>17.42</td>
<td>0.242</td>
<td>28.25</td>
<td>2.07</td>
</tr>
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</table>
formed heteropolar bonds of the Cu activities of the constituent elements (Ge, Se, and Cu) given in ref. [38] the glasses. The bond distribution may be used to get the bandgap of the 

\[ \Delta \chi = P_{A-B} |x_A - x_B| + P_{A-C} |x_A - x_C| + P_{B-C} |x_B - x_C| \]  

(11)

As the glass’s physical properties are correlated to the formed bonds, it is useful to calculate the degree of ionicity (\( I_{\text{on}} \)) of the glasses. According to Pauling [50], \( I_{\text{on}} \) can be calculated using the relation:

\[ I_{\text{on}} = 100 \left( 1 - \exp \left[ - \frac{\Delta \chi}{4} \right] \right) \]  

(12)

Fig. 5. The expected chemical bonds distribution for the Cu\(_{x}\)(Ge\(_{30}\)Se\(_{70}\))\(_{100-x}\) glasses.

Fig. 6. Plots of \( \Delta \chi, I_{\text{on}} \) and \( \text{Cov} \) versus Cu content for Cu\(_{x}\)(Ge\(_{30}\)Se\(_{70}\))\(_{100-x}\) glasses.

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The overall electronegativity difference could be estimated from the 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:

\[ \chi = \sum P_i (\chi_i - \chi) \]  

where \( P_i \) and \( \chi_i \) represent the proportion and energy gap of the \( i^{\text{th}} \) bond, respectively. This estimation takes into account the local surrounding of

\[ \chi = \sum P_i (\chi_i - \chi) \]  

where \( P_i \) and \( \chi_i \) represent the proportion and energy gap of the \( i^{\text{th}} \) 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$_{70}$Se$_{30}$)$_{1-x}$.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 properties of Cu$_x$(Ge$_{70}$Se$_{30}$)$_{1-x}$.x$ 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$_s$) increases with the enhancement of Cu in the Cu$_x$(Ge$_{70}$Se$_{30}$)$_{1-x}$.x$ glasses. The density ($\rho$) and compactness (s) of the system increases, whereas the mean atomic volume ($V_{ma}$) decreases with the enhancement of Cu amounts in the present glassy system. The increase of CE, H$_s$ and $\rho$ reflects the increase of the elastic moduli, Poason’s ratio and Deby’s temperature. The optical gap decreased from 2.21 eV for Ge$_{70}$Se$_{30}$ to 1.86 eV for Cu$_{30}$(Ge$_{70}$Se$_{30}$)$_{58}$ films, i.e. the wavelengths corresponding to $E_{g}$ values lie in the visible range of spectra, which make these films can be used in infrared applications. 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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