Effect of the Copper on Thermo - Mechanical and Optical Properties of S-Se-Cu Chalcogenide Glasses

Kavitha Samudrala and Suresh Babu Devarasetty*

1Department of Physics, Osmania University, Hyderabad, Telangana, India.

*Corresponding author E-mail: devarasetty1956@yahoo.co.uk

Abstract. The S\textsubscript{15}Se\textsubscript{85-x}Cu\textsubscript{x} (x = 0, 2, 4, 6, 8) chalcogenide glasses are synthesized using melt quenching technique and the effect of Copper on thermal, mechanical and optical properties of chalcogenide glasses are investigated. The glassy natures of the prepared samples were verified by X-ray diffraction and DSC studies. The optical band gap of the samples is estimated and it is observed that optical band gap is decreased with increasing of the copper content and is discussed in terms of cohesive energy and coordination number. The basic thermo-mechanical parameters such as micro-hardness, Volume (Vh) and formation energy (Eh) of micro voids in the glassy network and the modulus of Elasticity (E) are calculated in present glasses. The composition dependence of micro hardness is discussed in terms of heat of atomization energy.

1. Introduction
Chalcogenide glasses bear a noteworthy electrical and IR transmission properties which make them effective to be applied in the progress of threshold switching, memory switching, inorganic photoreceptor, IR Transmission, detection through lenses and optical waveguides [1, 2]. Moreover, the property reversible transformation that is being exhibited by Se alloys makes them pertinent in optical memory devices, X-ray imaging and photonics [3]. Selenium can melt within their structural units without any tangible transformation but with the required random arrangement of atoms being acquired by breaking the weak bonding between the units. The rearrangement into a crystal structure on cooling is a tough stage and that being the case, the glass can easily be formed. These studies imply that when S is incorporated to selenium (Se), it gets dissolved in the Se chains in order to satisfy its coordination requirements and forms a cross linked structure.

Optical properties and their experimental measurements symbolize one of the most considerable scientific activities in the domain of materials research. Based on properties such as refractive index and dispersion, which can be varied by varying chemical composition [4], glasses are being used in the preparation of optical instruments and lenses. One of the most distinguished applications based on optical properties of glasses is in the field of information technology via glass fibres. Furthermore, the absence of long range order allows the modification of their optical properties to a specific technological application through continuously changing their chemical composition.

The mechanical properties of these materials play a key role in practical applications and are connected intimately with their structure and other physical and chemical properties. Specifically, the hardness of glass is of direct practical significance as it is apparently connected to bonding in these materials. It has often been used as an approximate measure of strength [5, 6].

In the present work, the glasses S15Se85-xCu\textsubscript{x} were prepared through melt – quenching method and report the variations of optical band gap, refractive index and thermo-mechanical properties with Cu composition and discussed the results.
2. Experimental Method
In the present work, $S_{15}Se_{85-x}Cu_x$ ($x = 0, 2, 4, 6, 8$) glasses were prepared using melt quenching technique. The procedure of preparation of glass samples were presented in our previous paper [7]. The amorphous nature of the obtained samples were verified by XRD patterns, recorded using Philips X-pert pro X-ray diffractometer with CU-Kα radiation ($\lambda=1.54056\text{Å}$). The thermal behavior of the samples were investigated using DSC Q20 (TA Instrument) with 10mg powder at a heating rate of $10^\circ\text{C/min}$ under the protection of a flowing $N_2$ atmosphere. The absorbance spectra of samples were recorded by using JASCO V-670 (UV-VIS-NIR) spectro photo meter in the range of 200 to 1100 nm. The hardness of the samples was determined by using Vickers micro hardness tester UHLVMHT, HM-20 on polished samples.

3. Results and discussion
The XRD patterns of samples were shown in Figure 1. There are no sharp peaks observed in the patterns. Suggesting the amorphous nature of the samples

![XRD pattern](image)

**Figure. 1. XRD patterns of $S_{15}Se_{85-x}Cu_x$**

The DSC curve of the glass samples of $S_{15}Se_{85-x}Cu_x$ ($x= 0, 2, 4, 6, 8$) were shown in Figure 2. Glass transition temperature ($T_g$), onset crystallization temperature($T_c$) and peak crystallization temperature ($T_p$) were measured for all samples and presented in Table 1. As Cu atom has a larger atomic radius than that of Se and S atoms, the addition of Cu to S-Se lattice, makes the lattice to distort because of the disturbed Vander Waal atoms. The distortion in the lattice gives rise to three dimensional disorders in the material. Suggesting the addition and increase of Cu in S-Se system introduces structural changes.
Figure 2. DSC graphs of $S_{15}Se_{65-x}Cu_x$. 
### Analysis of UV-VIS-NIR absorption edges and optical band gap

Optical properties of chalcogenide glasses S-Se-Cu plays a significant role in understanding the optoelectronic nature. Figure 3 shows the optical absorption spectra of all samples. The optical absorption spectra of a glass samples reveal only one broad absorption band. Figure 3 shows that the absorption edges were not sharp, can be indicating the amorphous nature of the samples. Optical band gap energy cannot be determined accurately by using absorbance measurements alone. Escobar – ALARCOL, et.al [8] & Souri and Shomalian [9] proposed absorption spectrum fitting (ASF) method to find optical band gap more accurately.

| Code | Composition | \( T_g \) (K) \((\pm 0.01\text{K})\) | \( T_c \) (K) \((\pm 0.01\text{K})\) | \( T_p \) (K) \((\pm 0.01\text{K})\) |
|------|-------------|---------------------------------|---------------------------------|---------------------------------|
| Cu0  | \( S_{15} \text{Se}_{85} \) | 303 | 342.98 | 352.65 |
| Cu2  | \( S_{15} \text{Se}_{83}\text{Cu}_2 \) | 307 | 347 | 366 |
| Cu4  | \( S_{15} \text{Se}_{81}\text{Cu}_4 \) | 309 | 343 | 358 |
| Cu6  | \( S_{15} \text{Se}_{79}\text{Cu}_6 \) | 308 | 342 | 354 |
| Cu8  | \( S_{15} \text{Se}_{77}\text{Cu}_8 \) | 308.5 | 348 | 365.39 |

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**Figure 3.** Plot of absorbance vs wavelength (nm)
3.2 Absorption spectra fitting procedure:
In crystalline semiconductors, the relation between the absorption coefficient and incident photon energy can be obtained by the following equation [10, 11].
\[ \alpha(\nu) \nu = B (\nu - E_{gap})^m. \]  
Where \( E_{gap} \), \( B \) and \( \nu \) are the optical gap, constant and incident photon energy respectively and \( \alpha(\nu) \) (absorption coefficient) defined as \( \alpha(\nu) = \frac{2.303X Abs(\lambda)}{d} \), where \( d \) and \( Abs(\lambda) \) are the thickness of the sample and absorbance respectively. For more precise determination of \( \alpha \), it is necessary to perform corrections to the absorption due to reflection, also \( m \) is the index which can have different values of \( \frac{1}{2} \) (direct allowed), \( \frac{1}{3} \) (direct forbidden), 2(indirect allowed) and 3 (indirect forbidden) [12]. Equation (1) can be rewritten a function of wave length \( \lambda \).
\[ \alpha(\lambda) = B \lambda (\frac{1}{\lambda} - \frac{1}{\lambda_g})^m \]  
Where \( \lambda_g \) is the wavelength, \( h \) is the Plank’s constant and \( c \) is velocity of light. By substituting \( \alpha(\nu) \) value in equation (2) are gets
\[ Abs(\lambda) = B_1 \lambda (\frac{1}{\lambda} - \frac{1}{\lambda_g})^m + B_2 \]  
Where \( B_1 = [B (hc)^{m-\frac{1}{2}} \frac{d}{2.303}] \) and \( B_2 \) is a constant. Using above equation, one can calculate the optical band gap without any need of thickness of the sample. Thus the value of band gap, in electron volt can be calculated from the equation \( E_g = \frac{1239.83}{\lambda_g} \). The evaluated values of \( E_g \) of all samples are given in table (2). It is observed that the measured absorption data best fit to \( m=2 \) which corresponds to indirect allowed transition.

![Plot of (A/\lambda)^{1/2} vs 1/\lambda](image)

Figure. 4. Plot of \((A/\lambda)^{1/2}\) vs \(1/\lambda\).

3.3 The chemical bond approach (CBA)
The Optical band gap energy \( (E_g) \) is a bond sensitive property that indicates the strength of the formed bonds. The \( E_g \) values may be decreased due to either the changes in bond angles or bond lengths [13 - 15]. Table 2 shows that \( E_g \) values decreased with increase in Cu content. The variation of \( E_g \) values with Cu content can be explained using CBA. According to CBA model cohesive energy (CE) and the average coordination number is a function of Cu content. CE can be determined based on the expected bonds formed and their energies in S-Se-Cu system. It is found from [16] that the energies of bonds S-
Se > Se-Cu > Se-Se bonds. Hence in S-Se-Cu system S-Se bonds are formed first then Se-Cu bonds and at the end Se-Se bonds are formed.

The value CE can be calculated by using the following equation

$$CE = \sum \frac{N_i E_{B_i}}{100}.$$  \hspace{1cm} (4)

Where the expected amount of formed bonds and bond energy are represented by $N_i$ and $E_{B_i}$ respectively. The expected amount of formed bonds is given in Table 3. It is clear from the Table 2 that the CE values decrease with increase in Cu composition suggesting that the decrease in $E_g$ is due to decrease in CE.

3.4 Refractive index (n)

The refractive index n, which is a fundamental property for any optical material is closely associated with the electronic polarization of ions as well as local field present inside these optical instruments. Assessing the value of refractive index (n) significantly essential, particularly for those materials that can be used for the fabrication of optical devices. The following relation proposed by Dimitrov and Sakka is used for the evaluation of refractive indices (n) of the samples from the optical band gap ($E_g$).

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{20}{E_g}}.$$  \hspace{1cm} (5)

The obtained values are shown in table 2.

Table 2. optical band gap energy ($E_{\text{opt}}$ (ev)), refractive index (n), cohesive energy (CE) distribution of bonds

| composition | $E_g$ (ev) | n  | CE (Kcal / mol) | S-Se  | Se-Cu | Se-Se |
|-------------|------------|----|----------------|-------|-------|-------|
| Cu0         | 1.61       | 2.92| 81.04          | 0.1765| -     | 0.8235|
| Cu2         | 1.57       | 2.94| 79.71          | 0.1765| 0.0706| 0.7529|
| Cu4         | 1.56       | 2.95| 78.38          | 0.1765| 0.1412| 0.6823|
| Cu6         | 1.53       | 2.97| 77.05          | 0.1765| 0.2117| 0.6118|
| Cu8         | 1.45       | 3.02| 75.73          | 0.1765| 0.2824| 0.5412|

The obtained values are shown in table 2.

3.5 Thermo mechanical properties of S-Se-Cu chalcogenide glasses:
The Vickers hardness ($H_v$) mainly depends on strength of individual bonds and atomic packing density and it is a measure of micro-hardness of glass [17]. The micro-hardness ($H_v$) of all the samples were calculate the equation (6).

$$H_v = \frac{1854.4F}{d^2}. \quad (6)$$

Where the $F$ is applied load in kg and the $d$ is the length of the diagonal of the indentation is in mm.

Figure 5 shows the typical photographs of Vickers indented marks for $S_{15}Se_{85-x}Cu_x$. The evaluation of $H_v$ is done by using the average value of 10 indentation diagonals. Samples and the values are shown in Table. 4

![Figure 5](image_url)

**Figure 5.** Micro graphs of Vickers indent on surface of bulk samples of $S_{15}Se_{85-x}Cu_x$

The thermo-mechanical parameters volume of the micro voids ($V_h$), energy of micro voids ($E_h$), Elastic modulus ($E$) are calculated using the following equations.
$V_h = 3.58k \left( \frac{T_g}{H_V} \right)$.                                   (7)

$E_h = 3.58kT_g$.                                                      (8)

$E = 15H_V$.                                                          (9)

The estimated values of $V_h$, $E_h$ and $E$ for all samples are given in table 4.

The average coordination number $< Z >$ of the samples was calculated using the following equation.

$< Z > = \frac{\alpha N_S + \beta N_{Se} + \gamma N_{Cu}}{100}$.             (10)

Here, $\alpha$, $\beta$, $\gamma$ are the atomic percentages of S, Se, Cu and N$_S$, N$_{Se}$, N$_{Cu}$ are their respective coordination numbers. In the present glass system Cu has been introduced for Se. As the heat of optimization of Cu (338KJ/mol) is greater than that of Se (227KJ/mol). The value of $H_V$ is increased with increase Cu content. The greater heat of optimization of ternary alloy compared to that of parent binary alloy is probably the reason for its increase in the micro-hardness. The composition dependence of both $T_g$ and $H_V$ in terms of coordination number $< Z >$ is shown in Figure 6.

![Figure 6. Plot of $T_g$ vs $H_V$ against $<Z>$ for $S_{1.5}Se_{85.5}Cu_i$](image)

Further the composition dependence of volume ($V_h$) and formation energy ($E_h$) of micro-voids and modulus of elasticity E in terms of coordination number $< Z >$ is shown in Figure 7 and 8 respectively.
Figure 7. Plot of $E_h$ vs $V_h$ against $<Z>$ for $S_{15}Se_{85.3}Cu_x$

Figure 8. Plot of modulus of elasticity($E$) against coordination number
4. Conclusion
Melt quenching method is successfully used to prepare glasses of $\text{S}_{15}\text{Se}_{85-x}\text{Cu}_x$. The prepared samples are glassy in nature. Optical band gap energy decreased with increasing of the Cu content and is due to decrease in cohesive energy. The hardness of the samples increased with increasing the Cu content and it was discussed in terms of average heat of automatization energy. Thermo-mechanical parameters were estimated.

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