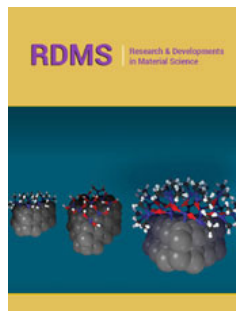


# Theoretical Model and Experimental Analysis for Optical Band Gap

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\*Corresponding author: Deepak Sharma,  
SCRIET, CCS University Meerut, India

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**Deepak Sharma\***

SCRIET, CCS University Meerut, India

## Abstract

Optical measurements were carried out on bulk glasses  $\text{Ge}_x\text{Se}_{1-x}$  ( $x = 10, 17, 22, 25, 33$ ). The direct band gap values were determined from the experimental data. Theoretical model is introduced which fits on the data. Compositional dependent power ( $p = 0.03$ ) on band gap data across the  $\text{Ge}_x\text{Se}_{1-x}$  series is determined. Duffy's relation is also explored to estimate the optical energy band gap which fairly matches with experimental band gap. Correlation graph between optical energy band gap ( $E_g$ ) and  $(1-R_M/V_M)$  shows a new relationship  $E_g = 7.58(1-R_M/V_M)^{1.08}$ . We are introducing the new concept of modified compactness for covalent glasses and composition dependent compactness across  $\text{Ge}_x\text{Se}_{1-x}$  glasses are understood. Physical parameters were also obtained such as chemical bond energy modification and cross-linking density (rigidity) in order to support the explanation of the optical band gap.

**Keywords:** Chalcogenide glasses; Rigidity; Band gap; Bond energy; Compactness; Model

## Introduction

Chalcogenide glasses are widely studied due to their interesting physical and optical properties. Chalcogenide glasses have a wide range of applications such as phase change memory devices, optical and electrical data storage, photovoltaic solar cells, xerography, optical fibre and fiber laser. An optical property plays a significant role in most of the applications of chalcogenide glasses. Among the chalcogenide glasses, Se based glass alloys in amorphous and crystalline forms which have found numerous applications based on optical and electrical properties [1]. Chalcogenide glasses can be used to develop better understanding of the glassy state, moreover pure selenium which is known to be the only element able to give monoatomic glass [2]. Heteropolar and homopolar bond formation in glasses can create compositional disorder, so compositional studies are important to enhance the understanding of the glassy material. Furthermore, compositional dependent increasing trend of binary alloys has been discussed in terms of rigidity parameter and experimental optical band gap is compared with theoretical model.

## Experimental

Bulk glassy samples were prepared from high purity (5N) elemental Germanium (Ge) and Selenium (Se). Germanium and selenium chunks were crushed to powders and equivalent ratios of compositions were weight and put into pre-cleaned ampoule. Bulk glasses were prepared from melt quenching technique. Ampoule was sealed under a vacuum pressure of  $10^{-6}$  Torr by a torch. The sealed ampoule was put in the thermal furnace; temperature was raised gradually in steps of  $25^\circ\text{C}$  in every ten minutes up to  $1000^\circ\text{C}$  and the temperature was monitored by placing a thermocouple at the ampoule position inside the furnace. Ampoule was held at this temperature for 24 hours. During the melting process the ampoule was periodically rotated thoroughly mix the alloy. After the end of 48 hours the ampoules were removed and immediately quenched in ice-water mixture to freeze the glassy structure. The ampoule was then broken to recover the glassy sample. The ingots were polished for optical

measurement. Polished samples were used to record UV-Visible transmission spectra.

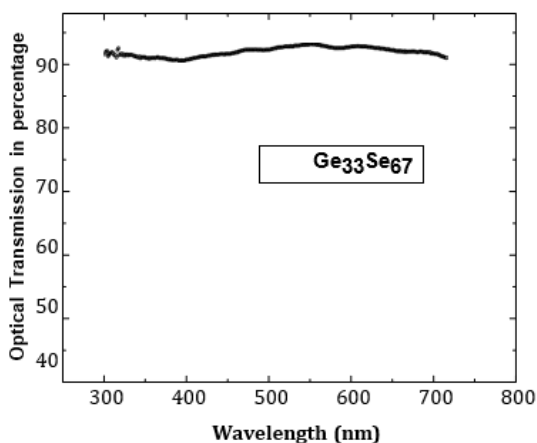
## Results and Discussion

Glasses do not have long range order; due to lack of periodic configuration at long range order, physics of glasses is still far behind to understand the peculiar nature of the material properties. Short range order in glassy material is nearly same as those of crystalline counterpart. Chalcogenide glasses are covalent in nature and obeying the so called 8-N rule, where N is the valency of an atom. According to this rule the number of nearest neighbor atoms for selenium (Se) and Germanium (Ge) are, respectively 2 and 4. The average coordination number  $\langle r \rangle$  of covalent bonds is a good measure representing the characters of atomic units [3].

The average coordination number  $\langle r \rangle$  for a binary sample can be expressed as:

$$\langle r \rangle = \frac{aX + bY}{X + Y}$$

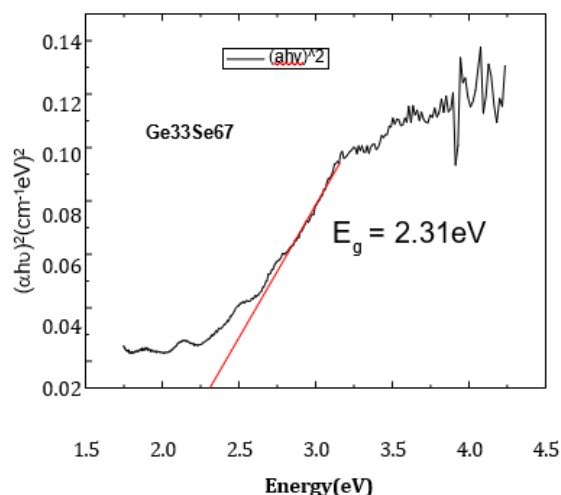
$a$  = coordination number of Ge and  $b$  is the coordination number of Selenium then for  $\text{Ge}_x\text{Se}_{1-x}$  glassy sample  $\langle r \rangle = 4x + 2(1-x) = 2x + 2$ . Network dimensionality  $D$  which is defined as number of dimensions where covalently bonded clusters can be extended, according to R. Zallen [4]  $D = 1$  and  $3$  respectively for amorphous selenium and germanium.  $D = 1$  for selenium corresponds to chain like morphology, in which entangled chain molecules are held together with weak intermolecular forces mostly consisting of Vander Waals type, and  $D = 3$  means three dimensional continuous-random networks.



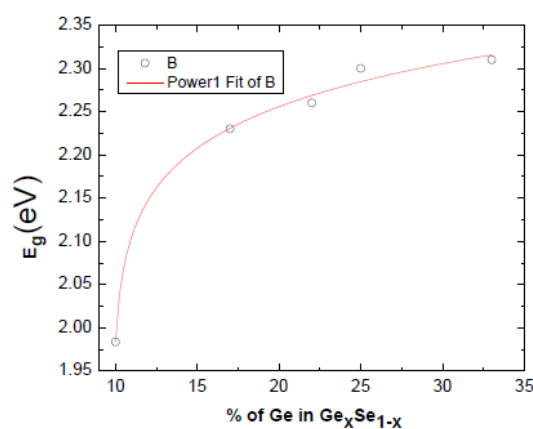
**Figure 1:** Optical transmission of  $\text{Ge}_{33}\text{Se}_{67}$  glass versus wavelength.

Figure 1 shows % of optical transmission as a function of wavelength for  $\text{Ge}_{33}\text{Se}_{67}$  composition. Selenium glasses possess a transmission range from 8-12 $\mu\text{m}$ , but tellurium glasses offer the widest infrared transmission [5]. Figure 1 shows very good transmission 92% in UV-Visible range, no scattering or absorption in this range. The variation of  $(\alpha h\nu)^2$  with photon energy  $h\nu$  for the same composition is shown in Figure 2. The value of optical direct band gap has been calculated by interpolating intercept on

X-axis as shown in Figure 2, same procedure has been adopted for other compositions and variation of band gap have been obtained for compositions. It is evident that the variation of optical band gap increases with increasing germanium percentage in selenium matrix up to  $\text{Ge}_{33}\text{Se}_{67}$  compositions/average coordination number as shown in Figure 3. The compositionally induced increasing trend of band gap may be understood as follows.



**Figure 2:** Direct band gap analysis for  $\text{Ge}_{33}\text{Se}_{67}$  composition.



**Figure 3:** Variation of band gap with fitted model across  $\text{Ge}_x\text{Se}_{1-x}$  glass series.

According to Linus Pauling [6] when the two atoms which differ in their electro negativity value, combine to form an alloy then the element of higher electro negativity (Selenium = 2.55, Germanium = 2.01) attracts an electron density towards itself when it bonds to another atom and behaves as an anion, whereas the other element behaves as a cation. The predicted produced bonds in the glasses under study, as per the chemical bond method, are Ge-Se, Se-Se, and Ge-Ge. The homopolar bonds Se-Se and Ge-Ge have bond energies of 184.1 KJ/mol and 188 KJ/mol, respectively. Ge-Se bond energies can be obtained in the following ways:

$E_{\text{Ge-Se}} = (E_{\text{Ge-Ge}} \times E_{\text{Se-Se}})^{1/2} + 30(X_A - X_B)^2$ ; where  $X_A$  and  $X_B$  are electro negativity of Ge and Selenium.  $E_{\text{Ge-Se}}$  is 193.53 KJ/mol based on the

computation above. Since Ge-Se has the highest bond energies, Ge-Se bonds will form first. It's been noted that this bond strategy ignores flaws like dangling bonds; these defects, along with the lesser Vander Waals forces' contribution to bond energy, result in linkages that are weaker than ordinary covalent bonds and further stabilize the structure [7]. The alloy's composition affects the glassy material's optical band gap. An optical band gap determination model is presented, with the compositional dependence form being as follows:

$$E_g(AB) = a|x - x_c|^p$$

The compositional distinctive attribute of this series, power  $p = 0.03$ , is determined from the fitted model over the series on the band gap as shown in Figure 3. On the other hand, Duffy [8] has obtained an empirical formula that relates energy gap  $E_g$  to molar refraction  $R_M$  and molar volume  $V_M$ ,

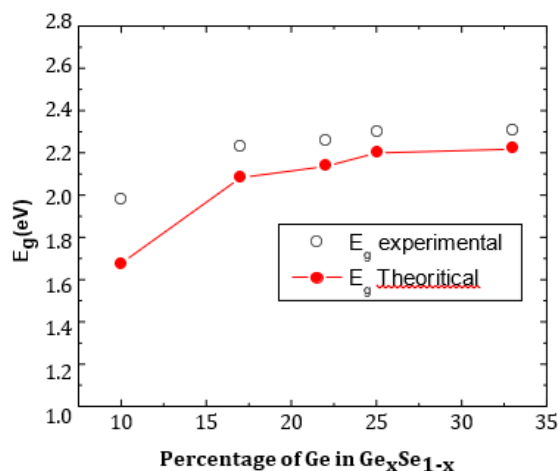
$$E_g = 20 \left( 1 - \frac{R_M}{V_M} \right)^2$$

The average molar refraction of isotropic materials for glasses is provided by this equation. The polarizability, or electrons' response to an applied field, is shown by the Lorentz-Lorentz equation. The volume ( $\text{cm}^3/\text{mol}$ ) parameter of the molar refraction  $R_M$ , the molar refraction  $R_M$  can be calculated as a function of polarizability  $\alpha_m$  when Avogadro number  $N_A$  is included.

$$R_M = 4\pi\alpha_m N_A / 3$$

with  $\alpha_m$  in ( $\text{\AA}^3$ ), the relationship between  $R_M$  and  $\alpha_m$  is transformed as  $R_M = 2.52\alpha_m$ .

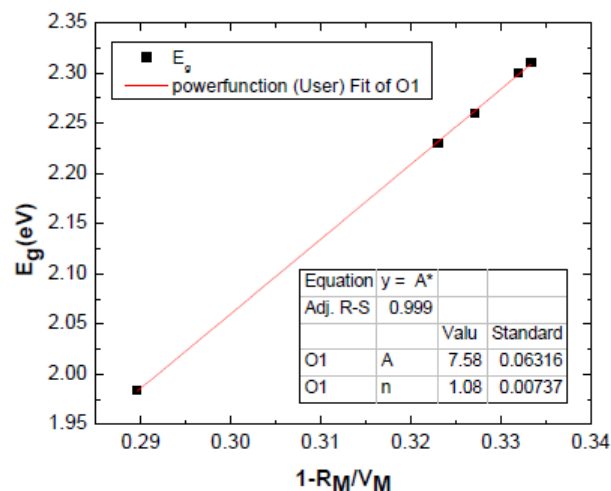
Theoretical optical band gap for  $\text{Ge}_x\text{Se}_{1-x}$  compositions has been computed and is displayed in Figure 4 alongside the experimental band gap; thus, the optical band gap theoretical and experimental results fairly agree. When we plotted  $E_g$  optical vs.  $(1-R_M/V_M)$ , we discovered a new correlation:



**Figure 4:** Theoretical and experimental band gap fairly matches across  $\text{Ge}_x\text{Se}_{1-x}$  compositions.

$$E_g = 7.58(1 - R_M/V_M)^{1.081}$$

as shown in Figure (5).



**Figure 5:** Correlation between  $E_g$  and  $1 - R_M/V_M$ .

The number of constraint  $N_c$  is calculated according to the relation:

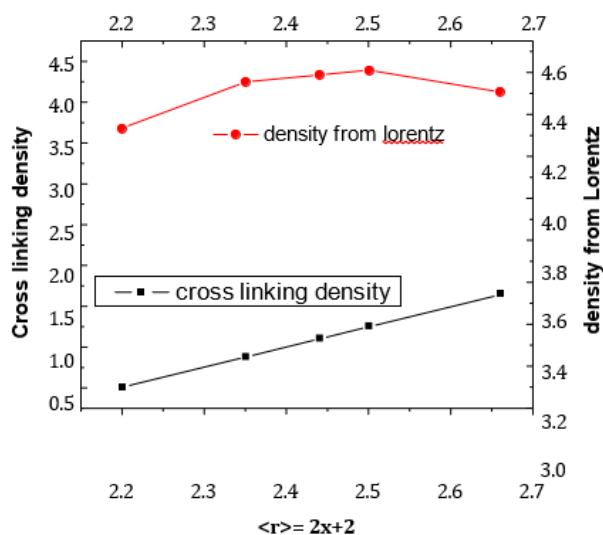
$$N_c = \langle r \rangle / 2 + 2 \langle r \rangle - 3$$

As the Germanium content in the Selenium matrix increases, so do the number of constraints  $N_c$  and the average coordination number  $\langle r \rangle$ . An increase in network cross-linking is associated with this growth. By rising the atomic proportion of germanium, the network's stiffness is reflected in both the average coordination number and  $N_c$ .  $\text{Ge}_x\text{Se}_{1-x}$  glasses are rigidly connected, where  $\langle r \rangle > 2.4$ . Based on the concept of average coordination proposed by Phillips [3] and Thorpe [9] glassy network consists of mixture of floppy and rigid regions. The glass network at  $\langle r \rangle = 2.4$  transform from floppy structure to rigid structure. The constraints number can be used to evaluate the cross-linking density ( $C_D$ ). Values of  $C_D$  were estimated from relation [10] according to:

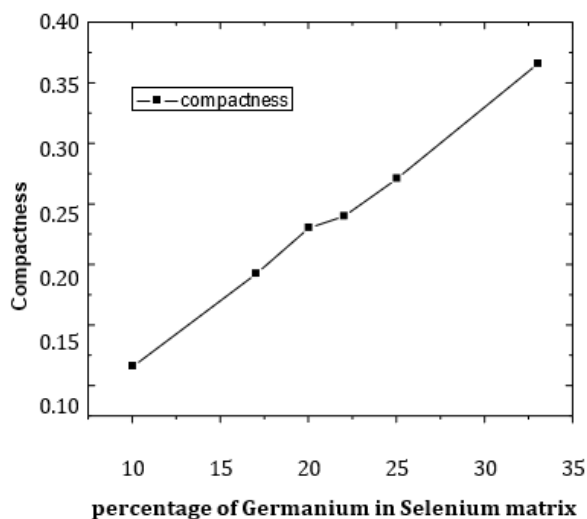
$$C_D = N_c - 2$$

The compositional dependency of the estimated cross-linking density and density from Lorentz are presented in Figure 6. Thus, compactness ( $\delta$ ) is reintroduced which is a measure of normalized change in cross-linking density with the composition glass density, hence, compactness  $\delta = \frac{\text{Cross-linking density}}{\text{Sample glass density}}$  quantity. Since all of the selenium is knotted with Germanium at the chemical threshold composition, there is no availability of free volume there at = 2.67 composition, as can be seen in Figure 6, which illustrates how cross-linking density increases with increasing germanium content. This indicates that the cross-linking density is a measure of rigidity in the composition. Figure 7 makes the compactness  $\delta$  quite evident. Rigidity and compactness are maximal at  $\langle r \rangle = 2.67$ , where rigidity completely percolates and all selenium is consumed by the germanium. At this value, 2D layered structures are fully evolved and rigidity and compactness are maximal. Initially, at very

low Germanium concentration, the network is floppy and isolated rigid regions are very small, so rigidity is very small. As the doping of Germanium concentration increases, the cross-linking increases, the free volume becomes smaller, so rigidity increases. Glasses have the highest chemical stability at  $\langle r \rangle = 2.67$  because they solely contain Ge-Se bonds. Because the system is the most compact, the Ge-Se bond energies are the biggest.



**Figure 6:** Cross linking density and density versus average coordination number.



**Figure 7:** Modified Compactness versus compositions across GeSe series.

## Conclusion

Optical direct band gap has been determined experimentally across the  $\text{Ge}_x\text{Se}_{1-x}$  compositions and theoretically band gap is estimated from Duffy's relation which is fairly fits with the compositions. Power model is also considered which fits the band gap and it gave us power  $p = 0.03$  over this series. A new correlation is also obtained for this glass series. We have introduced the new concept of modified compactness for covalent glasses and composition dependent are understood. We did not experimentally measured densities of the compositions, it is suggested that more elaborate studies are further necessary to measure experimental densities of the glasses.

## Declarations

This piece of work was performed without financial assistance, and the author has no conflicts of interest. The author is not a research competitor.

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