

MEASUREMENT OF OPTICAL DIFFUSION IN GE-SE- IN GLASSES

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ABSTRACT

The composition dependence of optical gap (E_g) in three sets of Ge-Se-In glasses, namely, $Ge_{10}Se_{90-x}In_x$ ($x = 5, 10, 15, 20$), $Ge_{15}Se_{85-x}In_x$ ($x = 0, 5, 10, 15, 20$) and $Ge_{22}Se_{78-x}In_x$ ($x = 4, 6, 10, 15$) have been studied by using rigidity percolation theory and bond constraints theory. E_g shows a local maxima at $\langle r \rangle = 2.67$. The result are discussed on the basis of the topological and rigidity theory exhibited by covalent network glasses. The relative sensitivity of E_g to these phenomena discussed.

I. INTRODUCTION

Chalcogenide glasses are generally P-type semiconductor and are expected to insensitive to the addition of impurities [1]. It has been found that the effect of impurities depend strongly on the composition of glass, the chemical nature of the impurity and the method of doping. Impurity concentration is a critical factor in such cases because all impurities cannot behave in an electrically active manner. Investigations on the influence of impurities on the properties of chalcogenide glasses are of relevance both from basic science and application point of view [2].

The Ge-Se-In ternary system is a prototypical chalcogenide glassy system and form bulk glasses over a wide range of composition expected up to 25% at %In and up to 60-90% at % Se with reminder being Ge [3].

Models based on chemical ordering [4] and network topology [5-8] has been proposed to explain the composition dependence of physical properties. The chemically ordered network (CON) model favors the formation of heteropolar bonds and thus the glass structure is composed of cross linked structure units of stable chemical compounds and excess, if any, of the elements. It has been argued that chemical ordering leads to a chemical threshold at which specific features in the composition dependent variations occur [9]. The topological model is based on balancing the number of operative constrains with the number of degree of freedom. This model describes the composition dependence in terms of the average coordination number $\langle r \rangle$ and predicts a topological threshold at $\langle r \rangle = 2.4$, where the rigidity of the network percolates [10]. The network is floppy below $\langle r \rangle = 2.4$ and rigid above $\langle r \rangle = 2.4$. A later modification of this model [11] based on the formation of two dimensional layer structures and medium range interactions suggests a topological threshold at $\langle r \rangle = 2.67$ where a change from two dimensional layered structure to three dimensional network takes place due to cross linking.

The applicability of the ideas of rigidity percolation was verified in many binary and ternary glasses [12-13]. Signature of rigidity percolation has been reported to occur at 2.4 or near 2.67 in various glasses.

In this paper , we present results on the composition dependence of optical energy gap in three sets of Ge-Se-In glasses , namely $\text{Ge}_{10}\text{Se}_{90-x}\text{In}_x$ ($x = 5, 10, 15, 20$), $\text{Ge}_{15}\text{Se}_{85-x}\text{In}_x$ ($x = 0, 5, 10, 15, 20$) and $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$ ($x = 4, 6, 10, 15$). The composition range covers the threshold composition predicted on the basis of various models .In terms of average coordination number $\langle r \rangle$, calculated using the formula-

$$\langle r \rangle = \frac{[(X)Z_{\text{Ge}} + (Y)Z_{\text{In}} + (100-X-Y)Z_{\text{Se}}]}{100}$$

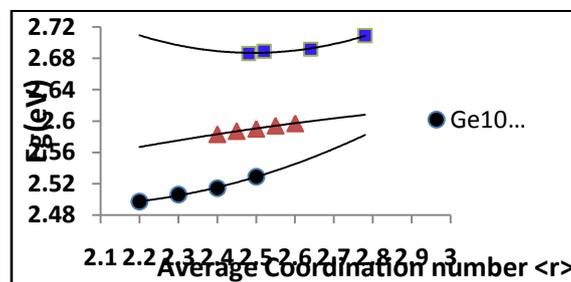
Where $Z_{\text{Ge}} = 4$, $Z_{\text{In}} = 4$ and $Z_{\text{Se}} = 2$ are the coordination number of Ge, In and Se respectively the compositions fall in the range $2.20 \leq \langle r \rangle \leq 2.78$.

II.EXPERIMENTAL

The glass formation region for Ge-Se-In consists of two islands [14]. The samples were prepared using the conventional melt-quenching technique. Appropriate amounts of high purity(99.999%) constituent elements were sealed in a quartz ampoule at about 10^{-3} Pa and loaded in a rotary furnace . The ampoule was kept at 1000°C for 12h with a continuous rotation for homogenizing the mixture. It is then quenched in a mixture of NaOH and ice water. The glassy nature of the sample was confirmed by X-ray diffraction technique.

III.RESULTS AND DISCUSSION

The variation of optical energy gap E_g as function of average coordination number $\langle r \rangle$ for the three sets of glasses studied is given in Fig.- 1. It can be inferred that the three sets of glasses show identical trends in the $\langle r \rangle$ dependence. E_g increases initially $\langle r \rangle$ is increased and then exhibit a local maximum at $\langle r \rangle = 2.67$. An explanation of the observed behavior can be given in the framework of the energy band model for the chalcogenide glasses proposed by Kastner [15] and the change in the average bond energy of the system as the composition varied. According to the Kastner the valance band in the chalcogenide glasses is constituted by the lone-pair bands where the conduction band arises from the anti-bonding band. In a multi-component glass like Ge-Se-In the position of conduction and valance band edges and thus the energy gap largely depends on the relative number of various possible bonds in the system and the average bond energy. The various possible bonds in the Ge-Se-In system are Ge-Se, Se-Se, Se-In, Ge-Ge, Ge-In and In-In . The bond energies are 231.11, 189.22, 257.5, 185, 146.06, and 217kJ/mol respectively



**Fig.-1 Variation of Optical Gap (E_g) With Average Coordination Number $\langle R \rangle$
For The Three Sets of Ge-Se-In Glasses**

The observed initial increase in E_g with increase in $\langle r \rangle$ suggests that in this region of curve the influence of the relative number of Se-Se and In-In bond are less prominent in determining the band gap than that of the GeSe_2 structural unit. It appears that Ge-Ge bonds are present in all these compositions. The increase in E_g continuous under the influence of the relative decrease in the number of strong Ge-Ge bonds.

The composition with $\langle r \rangle = 2.67$ contains a large concentration of relatively strong In-In bonds resulting in a increase in E_g . However, it may be mentioned that $\langle r \rangle = 2.67$ also corresponds to the topological threshold suggested by Tanaka [8] based on the formation of a layered structure and medium range interactions.

IV .CONCLUSION

The variation of E_g of the three sets of Ge-Se-In glasses studies show features at different $\langle r \rangle$ values. These results can be interpreted as a signature of two different phenomena occurring in this system, namely, the chemical threshold and the topological threshold Since E_g is more sensitive to variations of the relative number of different bonds and the average bond energy of the system. The local maximum in the E_g variation is the signature of the chemical ordering occurring in the system at $\langle r \rangle = 2.67$. Hence both chemical and topological threshold exhibit in the Ge-Se-In system and manifest in the properties that are sensitive to either of the phenomena.

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