Measurement of Optical Diffusion in Three sets of Ge-Se-In Glasse

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Abstract:- The composition dependence of optical gap (E_g) in three sets of Ge-Se-In glasses, namely, $(GeSe_4)_{1-x}In_x$ $(GeSe_5)_{1-x}In_x$ and $(GeSe_6)_{1-x}In_x$ where x = 0,5,10,15,20 have been studied by using rigidity percolation theory and bond constraints theory. E_g shows a local maxima at <r> = 2.67. The results 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.

INTRODUCTION

Chalcogenide multicomponent glasses have attracted significant attention due to their remarkable optical properties and technological applications [1, 2]. They are considered as typical glasses for infrared applications [3, 4] and provide good candidates for photo-structural optical recording [5], acousto-optic devices [6, 7] and advanced IR optical fibers [8]. They also provide solid-state physicists with new solutions for the challenging fundamental problems that relate to the possible technological applications for these glasses [7, 9]. The Ge–Se–In system is of special interest in view of the fact that it forms glasses over a wide domain of compositions extending to about 60–90 at.% of Se atoms and about 15 at.% In, with the Ge atoms as remainder [10–13]. Therefore, it is considered as a suitable model system for the investigation of the variation of certain physical properties with composition or equivalently with the average coordination number [14,15].

Since the addition of a third alloying element has pronounced effect on the structural and physical properties, we propose in this paper to study the role played by metallic indium on the covalently bonded Ge–Se glasses. Several authors have studied the optical properties of the formed ternary compounds. Through investigations, researchers have shown the effect of In addition on the optical and energetic properties of the Ge–Se glasses which create both compositional and configurationally disorders in this system.

Decreasing the band gap of a material due to metal impurities has been approved through several studies, and this subject is considered as a major area of interest within the optoelectronic applications. Indium-based chalcogenides have been considered good candidates in nonlinear optics due to their ability to transmit in the infrared region. The aim of present investigation is to understand the role of chemical composition and

mean coordination number in determining their structural, physical and optical properties.

RESULT AND DISCUSSION

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 [16]. Models based on chemical ordering [17] and network topology [18,21] 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 [22]. 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 <r> and predicts a topological threshold at <r> = 2.4, where the rigidity of the network percolates [23]. The network is floppy below <r>=2.4 and rigid above <r> = 2.4. A later modification of this model [24] based on the formation of two dimensional layer structures and medium range interactions suggests a topological threshold at <r>= 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 [25,26].

Signature of rigidity percolation has been reported to occur at 2.4 or near 2.67 in various glasses.
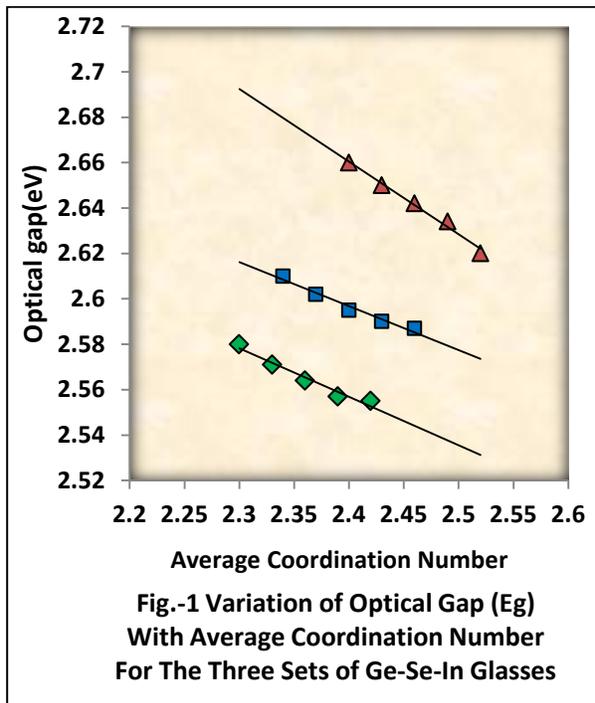
In this paper, we present results on the composition dependence of optical energy gap in three sets of Ge-Se-In glasses, namely $(GeSe_4)_{1-x}In_x$, $(GeSe_5)_{1-x}In_x$ and $(GeSe_6)_{1-x}In_x$ where x = 0, 5,10,15,20. The composition range covers the threshold composition predicted on the basis of various models .In terms of average coordination number <r>, calculated using the formula-

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

Where $Z_{Ge} = 4$, $Z_{In} = 4$ and $Z_{Se} = 2$ are the coordination number of Ge, In and Se respectively the compositions fall in the range $2.20 < (r) < 2.78$.

The variation of optical energy gap Eg as function of average coordination number <r> 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 <r> dependence. Eg decreases initially <r> is increased and then exhibit a local maximum at <r> = 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 (Eg) With Average Coordination Number For The Three Sets of Ge-Se-In Glasses

The observed initial decrease in Eg with increase in <r> suggests that in this

region of curve the influence of the relative number of Se-Se and In-In bond are strong prominent in determining the band gap than that of the GeSe2 structural unit. It appears that Ge-Ge bonds are present in all these compositions. The decrease in E_g continuous under the influence of the relative increase in the number of strong Ge-Ge bonds.

CONCLUSION

The variation of Eg of the three sets of Ge-Se-In glasses studies show features at different <r> 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 Eg 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 Eg variation is the signature of the chemical ordering occurring in the system at <r> = 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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