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Optical properties of bismuth doped Ge-Se glass system

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Optical studies have been performed on alloyed samples of [Ge_{20} Se_{80-x} Bi_x (x = 0, 2.5, 4, 6)] prepared by conventional melt quenching technique. The glass transition temperatures of the given glass system are evaluated using Modulated Differential Scanning Calorimetry [MDSC]. Optical absorption measurements showed that the fundamental absorption edge is a function of composition. The energy gap (E_g) decreases with the increase of Bi content and variation of the optical band gap with the compositions is also studied.

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1. Introduction

Ternary compounds of chalcogenide glasses find wide range of applications. Because of laser-induced memory effect in these materials, recent research has been devoted to the development and investigation of chalcogenide materials suitable for optical recording. They are also used as core material for optical fibers for transmission in the range 6 – 12 μm, especially when short lengths and flexibility are required [1-4]. Chalcogenide semiconductors have truly emerged as multipurpose materials and have been used to fabricate technological important devices such as infrared detector, electronic and optical switches and optical recording media [5]. Chalcogenide glassy semiconductors are normally p-type and the added impurities do not alter its p-type conduction, but the addition of Bismuth (Bi) in large concentrations [≥ 11 at %] in Ge based glasses can switch the conduction from p to n type [6]. The most stable Bi chalcogenide glasses have been found [7] to contain 20-30 % of germanium and less than 20 % of bismuth. The addition of Bi was found to affect the optical properties of these types of glasses [8]. The study of the optical absorption and particularly the absorption edge is useful for investigation of optically induced transitions and for the provision of information about the band structure and energy gap in both crystalline and non-crystalline materials [9]. There are two kinds of optical transitions at the fundamental edge of crystalline and non-crystalline materials, direct transition and indirect transition; both involve the interaction of electromagnetic wave with an electron in the valence band, causing the transition across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band it is essential for the wave vector of the electron to be unchanged. In the case of indirect transitions the interactions with lattice vibrations takes place

The present study is undertaken to investigate the influence of composition on the glass transition temperature and the optical properties of chalcogenide glass system Ge_{20} Se_{80-x} Bi_x [with x = 0, 2.5, 4, 6].

2. Experiments

Ge_{20} Se_{80-x} Bi_x glasses (x =2.5, 4, 6) are prepared by melt quenching technique. High purity (99.999%) materials are weighed according to their atomic percentage and are sealed in quartz ampoules at a vacuum of 10^{-5} torr. The sealed ampoules are kept inside the furnace and the temperature is raised to 950^0C at the rate of 3 to 4 K min^{-1}. The ampoules are frequently rocked for 24 hours at the maximum temperature 950^0C to make the melt homogeneous. The ampoules are then quenched in ice water. The amorphous nature of the glassy system is confirmed with XRD. MDSC studies are conducted using a TA MDSC 2910 calorimeter; with the baseline correction applied using an empty pan. The calibration for enthalpy and temperature is done with high purity indium and the calibration for specific heat has been undertaken using high purity sapphire. The sample around 8-16 mg in weight is grounded in to a fine powder and sealed in an Al pan. An empty Al pan is taken as reference. Samples are equilibrated initially at 30^0C for 2 minutes and the MDSC experiment are carried out at a heating rate of 5^0C $min^{-1,}$ with the modulation amplitude of $\pm$1.5 ^{0}C and the modulation period of 60s. The reversing and non-reversing heat flows through the glass transformation region during both heating and cooling schedules in the temperature region 80-400^0c are measured and the glass

transition temperature T_g, of the thermal events in the glass transition region are determined.

Absorption measurements in the wavelength range 300 - 900 nm are carried out using a double beam spectro photometer [Varian D M S].

3. Results and discussion

Fig. 1 shows the variation of glass transition temperature, T_g with Bismuth (Bi) concentration at a heating rate of 10K/min. The increase in T_g with increase of Bi content can be explained in line with the argument of Bhatia et.al [6].

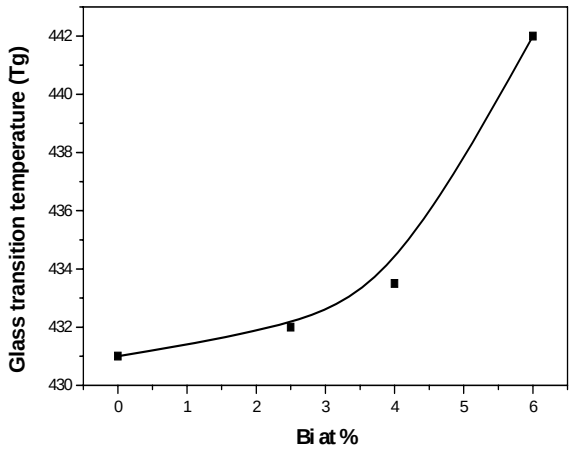

Fig. 1. Variation of glass transition temperature with Bi content.

As the Bi percentage increases, it enters in to the chain forming Bi-Se bonds. The addition of Bi at the expense of Se concentration, which enters into $(Se)_n$ chains connecting the tetrahedral units may also cross-link the chain. This cross-linking further strengthens the bond structure and therefore accounts [9] for the increase of T_g with the increase of Bi content. Bi doped chalcogenide glasses show carrier type reversal from p to n type. This is also explained on the basis of bismuth doping. At higher percentage of Bi, the dopant atoms enters into the tetra hedral units $(GeSe_{1/2})_4$ and induce a modification in the host semiconductor which moves the Fermi level towards the conduction band making it n–type semiconductor. Thus the addition of Bi relatively increases the Ge concentration with respect to Se and hence Ge–Bi bonds are favored [10, 11, 12] instead of Se- Bi bonds. As the number of covalent bonds per atoms for Ge is four and for Se is two, the increased Bi-Se bonds are expected to produce [12] a more compact structure. This type of structural modification may account for increase of T_g as observed in this glassy system.

The optical band gap (E_g) of amorphous semiconductors is usually determined [13, 14] from the part of the absorption edge, where the density of state variation is significant, ie, where the following relation holds

$$\alpha h\nu = A(h\nu - Eg)^m \quad (1)$$

where **α** is the absorption coefficient, **ν** is the frequency and **m** is a number characterizing the optical absorption processes having a value ½ for the direct allowed transition and value of 2 for indirect transition. The absorption coefficient is calculated as a function of photon energy from absorbance versus wavelength curve. The plots of $(\alpha h\nu)^2$ versus hν (Fig. 2) and $(\alpha h\nu)^{1/2}$ versus hν (Fig. 3) are used to evaluate the optical band gaps for the direct and indirect transitions. Direct $E_g(d)$ and indirect $E_g(i)$ transitions the energy gaps of the given $Ge_{20}Se_{80-x}Bi_x$ glass system with different compositions are determined by the intercept of the extrapolations to zero absorption with the photon energy axis. The values of direct and indirect energy gaps thus obtained are listed in Table 1.

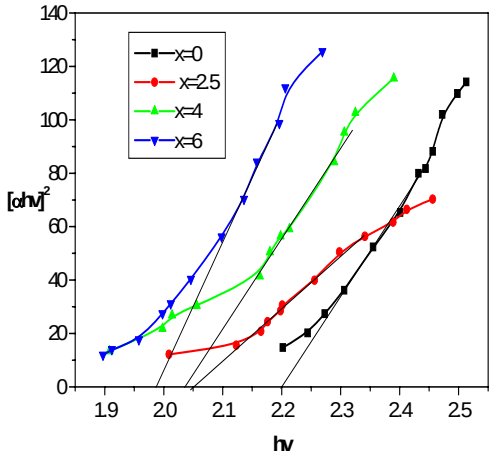

Fig. 2. Variation of $(\alpha h\nu)^2$ with hν for $Ge_{20}Se_{80-x}Bi_x$ (x= 0,2.5,4 & 6) glass system.

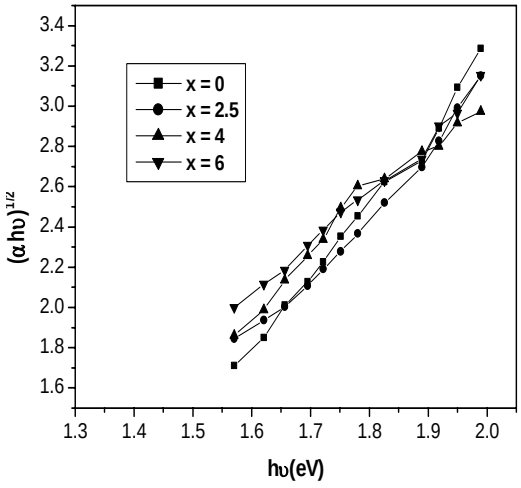

Fig. 3. Variation of $(\alpha h\nu)^{1/2}$ with hν for $Ge_{20}Se_{80-x}Bi_x$ (x= 0,2.5,4 & 6) glass system.

Table 1.Variation of glass transition temperature (T_g) direct $E_g(d)$ and indirect band gap $E_g(i)$ with Bi content

$Ge_{20}Se_{80-x}Bi_x$	Glass transition temperature (Tg)[K]	E_g(d)[eV]	E_g(i) [eV]
x=0	431	2.201	1.536
x= 2.5	432	2.051	1.521
x=4	433.5	2.033	1.515
x=6	442	1.985	1.448

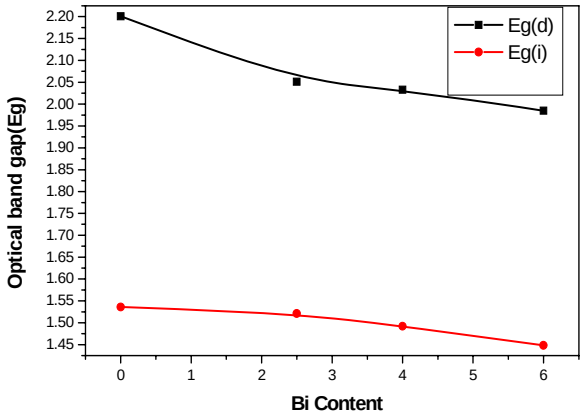

Fig. 4. Variation of direct $E_g(d)$ and indirect band gap $E_g(i)$ with Bi content.

It is seen that E_g decreases with increasing Bi content. This trend indicates the increasing density of localized states within the band gap as suggested by Davis and Mott. [14]. The decrease of optical band gap with increasing Bi content is related to the increase of Bi- Se bonds and the decrease of Se- Se bonds. Bi enters in to the tetrahedral structure $GeSe_2$ forming units containing all the three elements (Ge, Se, Bi), thus leading to the modification of the glassy network. The decrease in the optical band gap is qualitatively in agreement with the concept that a decreasing ionic character of the covalent bond leads to a small energy gap of the corresponding material of the system. The variation of optical band gap with Bi content is shown in Fig. 4.

4. Conclusions

The introduction of Bi in to the Ge-Se glass system results in the modification of the glass network by the creation of Ge-Se-Bi linkages. The study of the optical properties of the $Ge_{20}Se_{80-x}Bi_x$ (x = 0, 2.5, 4, 6) glass system shows that the value of the direct and indirect optical band gap decreases with increasing Bi content. This decrease in both the optical band gaps with increasing Bi content is related to the increasing density of localized states within the band gap and it is also related to the increase of the Bi – Se bonds and the decrease of Se – Se bonds.

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