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Optical study of thin Film of cgs $Ge_{10}Se_{90-x}Bi_x$

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Abstract: The optical band gap increases up to 2% of Bi concentration in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) with further increase of Bi content the optical band gap decreases in the present system. The increase in the optical band gap with increasing Bi content may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands). The values of optical band gap (E_g) decrease at higher Bi concentration. Since the optical absorption depends on the short-range order in the amorphous state and defects associated with it. The decrease in the optical band gap in the present system may be due to deduction in the amount of disorder in the system and increase in the density of defects state

I. INTRODUCTION

Chalcogenide glasses have been studied intensively in the last few decades owing to their interesting properties and technological applications. Therefore much work has been done on both bulk and thin films formed of glassy chalcogenides regarding electrical and optical properties [1-3].

Vitreous Te-based alloys have recently been the subjects of extensive work; with an emphasis on structural changes because of new technological applications particularly in the field of optical data storage [4]. Many studies devoted to the diversification (i. e. the crystallization from the vitreous phase) of binary X-Te [5-8]; or ternary X-Y-Te vitreous alloys [9-11]. For all these systems, the glass-forming region is often located in the Te rich range, and during annealing most of these glasses exhibit double glass-transitions. Differentials scanning calorimetric (DSC) studies have been carried out on germanium telluride glasses containing Cu and Ag by Ramesh *el al* [12]. On the basis of the diversification behavior of these glasses they concluded that the network connectivity of the parent Ge-Te matrix is not improved by the addition of Cu. The thermal stability of some ternary compounds of the $Cu_xGe_{0.2}Te_{0.8-x.}$ type has been evaluated by Vazquez *et al* [13]. Electrical resistivity measurements under pressure at ambient and low temperature has been carried out [14] on bulk melt quenched Cu_x Ge_{15},Te_{80-x} glasses. The resistivities of these samples are found to decrease continuously with pressure, changing by about six orders of magnitude around 4 G Pa pressure.

The variation of conductivity activation energy with pressure also confirms the continuous metallization of Cu-Ge-Te samples. The composition dependence of properties such as resistivity is found to exhibit anomalies at the composition 5 at % Cu. These results are explained on the basis of the rigidity percolation in chalcogenide network glasses. Most of the reported papers were focusing on crystallization kinetics in the Cu-Ge-Te glassy system [15-16]. In our work, the effect of incorporation of Bismuth in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films were studied by measuring the optical absorption, reflection and transmission. The optical energy gap (E_g) of different samples of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) at room temperature was reported. The changes of E_g and the increase of the width of localized states E_e were attributed to the amorphous- crystalline transformation. El-Zahed [17] studied the optical absorption of Cu_x Ge_{20-x} Te_{80} films as a function of composition (x = 0, 1.5, 3). In the present studied we have studied the absorption coefficient (α) as a function of incident photon, variation of $(\alpha h\nu)^{1/2}$ with photon energy, variation of reflectance (R), variation of transmittance (T), changes in refractive index (n) and extinction coefficient (k) with the photon energy, and finally the real (ε'_r) and imaginary (ε''_r) parts of the dielectric constant for all the two samples with the concentration variation of Bi and Se. The study shows that, the mechanism of the optical absorption follow the rule of direct transition.

II. EXPERIMENTAL

Glassy alloys of $Ge_{10}Se_{90-x}Bi_x$ (x = 0, 2, 4, 6, 8, 10 and 20) were prepared by quenching technique. The exact proportion of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm. The materials were then sealed in evacuated (~10^{-5} Torr) quartz ampoules length ~ 6 cm and were internal diameter ~ 8 mm). The sealed ampoules containing were heated to 950^0C and were held at that temperature for 10 hours inside a furnace. The temperature of the furnace was raised slowly at a rate of 3-4^0C / minute. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod o which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by x-ray diffraction patterns.

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~500 nm. The coplanar structure (length~1.2 cm and electrode separation~0.5 mm) was used for present measurements.

The electrical conductivities in dark as well as in presence of light were studied by mounting them in a specially designed sample holder in which illumination could be achieved through a transparent window. A vacuum of about 10^{-4}Torr was maintained throughout these measurements. The temperature of the film was controlled by mounting the heater inside the sample holder and measured by a calibrated chromul alumel constantan thermocouple mounted very near to the films. The heating rate was kept quite small (0.5 K/min.) for these measurements.

III. RESULTS AND DISCUSSION

The variation of the absorption coefficient (α) as a function of incident photon energy (hν) for deposited thin films of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) at 125^0C temperature are shown in Fig. 1. The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curves using the relation [18-19],

$$\alpha = OD/\,t \qquad \ldots (1)$$

Where OD is the optical density measured at a given layer thickness (t) and layer thickness is 500nm.

It has been observed that the value of absorption coefficient (α) increases linearly with the increase in photon energy for all the samples of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) system.

In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to either of the three processes (i) residual below-gap absorption (ii) Urbach tails and (iii) interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges which are relatively insensitive to preparation conditions and only the observable absorption [20] with a gap under equilibrium conditions account for process (i). In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation [21]. In crystalline materials the fundamental edge is directly related to the conduction and valance band, i.e. direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is observed. In these materials, α increases exponentially with the photon energy near the energy gap. This type of behavior has also been observed in many other chalcogenides [22]. This optical absorption edge is known as the Urbnch edge and is given by,

$$\alpha \sim \exp [\ A(h\nu - h\nu_0)]/kT \qquad \ldots (2)$$

Where A is a constant of the order of unity and ν_0 is the constant corresponding to the lowest exciting frequency.

In the various absorption processes, the electron and the holes absorb both a photon and a phonon. The photon supplies the needed energy, while the phonon supplies the required momentum. The variation of α with photon energy can be explained in term of: (i) fundamental absorption (ii) excitation absorption and (iii) valance band acceptor absorption. The exact calculated values of the absorption coefficient (α) are given in the Tables 1 for $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) In case of $10^4 \le \alpha \le 10^6$ cm^{-1} in the high absorption region (where absorption is associated with interband transition)Tauc and Davis and Mott independently derived an expression relating the absorption coefficient α to the photon energy hν

$$\alpha h\nu = \beta\{ h\nu - E_g\}$$

$$\beta = (4\pi\sigma/ncE_c)$$

The present system of alloys obey the role of non-direct transition (m >1) and the relation between the optical gap, optical absorption coefficient α and the energy hν of the incident photon is given by [23-28],

$(\alpha\, h\nu)^{1/2} \propto (h\nu - E_g)$ … (3)

Table 1. Variation of the Band gap with different samples of a- $Ge_{10}Se_{90-x}Bi_x$ (where x=0,2,4,6,8,10 & 20)at room temperature and 125^0C temperature.

Band Gap in (ev) at 125^0 C						
$Ge_{10}Se_{90}$	$Ge_{10}Se_{88}Bi_2$	$Ge_{10}Se_{86}Bi_4$	$Ge_{10}Se_{84}Bi_6$	$Ge_{10}Se_{82}Bi_8$	$Ge_{10}Se_{80}Bi_{10}$	$Ge_{10}Se_{70}Bi_{20}$
1.24	1.32	1.118	1.12	1.1	1.08	1.01

The variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) for $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) films respectively are shown in Fig. 2.

The variation of extinction coefficient (k) and reflectance (R) in percentage for the present system of $Ge_{10}Se_{90-x}Bi_x$ are shown in Fig.3 and 4 respectively. These figures show that the extinction coefficient (k) and reflectance (R) increases with wavelength in all the seven samples. The refractive index (n) and extinction coefficient (k) have been calculated by using the phenomenon of reflection of light for the set of the samples discussed above. The variation of refractive index (n) and the transmittance (T) also has drawn for $Ge_{10}Se_{90-x}Bi_x$ in the Fig. 5 & 6 respectively. The spectral dependence of refractive index (n) shows a constant variation. It is also clear from the graphs of the transmittance that the percentage in the transmission increases in all the samples with respect to the wavelength. A clear cut peaks are also observed in the transmission spectra in all samples of $Ge_{10}Se_{90-x}Bi_x$ which indicates that the values of the transmission starts decreasing after about 600 nm in these samples.

$T = [(1-R)^2 e^{-\alpha d}/1-R^2 e^{-2\alpha d}]$

According to this theory, the reflection of light from a thin film can be expressed in term of Fresnel's coefficient. The reflectivity [29-31] on an interface can be given by ;

$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2]$ … (4)

and $\alpha = 4\pi\, k / \lambda$ … (5)

where λ is the wavelength.

The value of refractive index (n) increases with increasing the photon energy and the value of transmittance coefficient (T) increases with increasing the wave length.

The real (ε'_r) and imaginary (ε''_r) parts of the dielectric constant for $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films have also been calculated at room temperature by using the following relations.

$\varepsilon'_r = n^2 - k^2$ and $\varepsilon''_r = 2nk$ … (6)

The variation of real (ε'_r) and imaginary part (ε''_r) of the dielectric constants with photon energy are plotted in the Fig. 7 and Fig. 8 for $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films respectively.

The value of indirect optical band gap (E_g) has been calculated by taking the intercept on the X-axis to zero absorption with the photon energy The calculated values of E_g for all the glassy samples of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) with and without annealing are given in Table – 17. It is evident from this table that the value of optical band gap (E_g) increases from 1.37 to 1.50 with increasing Bi content in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) at room temperature and from 1.01 to 1.32 with increasing Bi content in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) after annealing the sample at 125^0C temperature respectively. The increase in the optical band gap with increasing the Bi contents in all the alloys may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands). The values of optical band gap (E_g) also decreases at certain points in the samples at room temperature and the annealed samples with change in concentration of Bi. Since the optical absorption depends on the short-range order in the amorphous state and defects associated with it. The decrease in the optical band gap in the present system may be due to reduction in the amount of disorder in the system and increase in the density of Defects State.

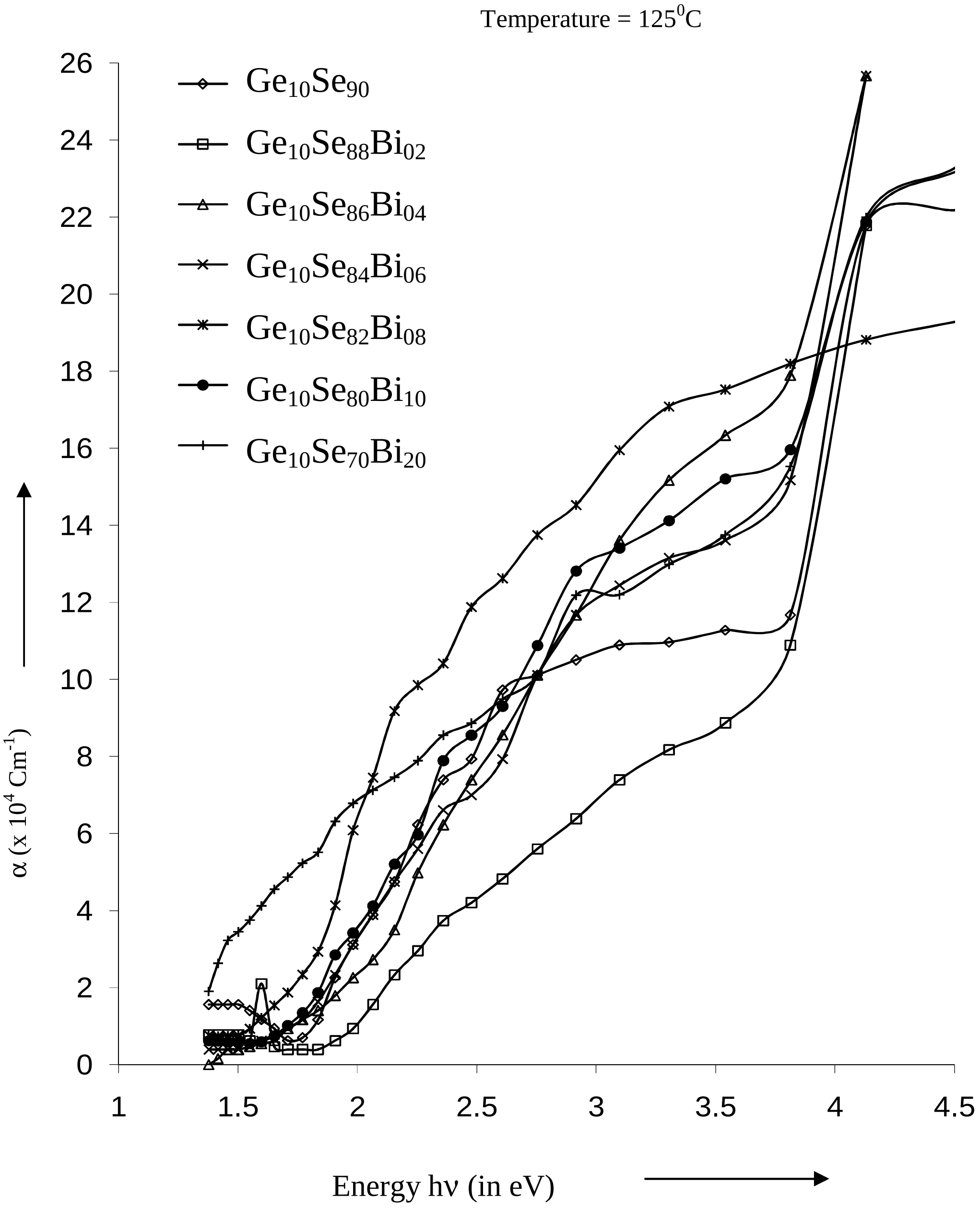

Fig. 1. Variation of Absorption coefficient (α) with photon energy in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^{0}C.

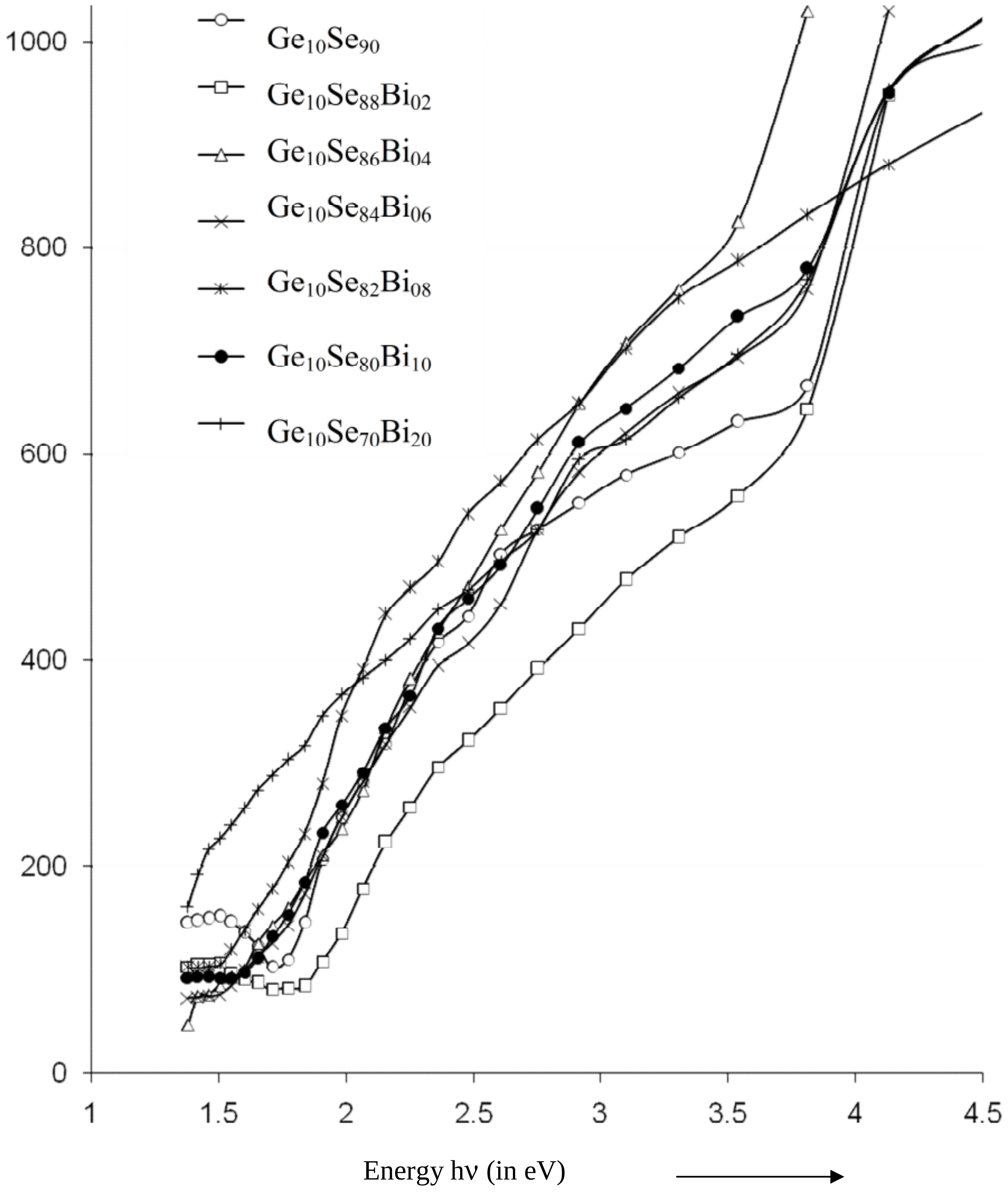

Fig. 2. Variation of $(\alpha h\nu)^{1/2}$ with photon energy in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^0C.

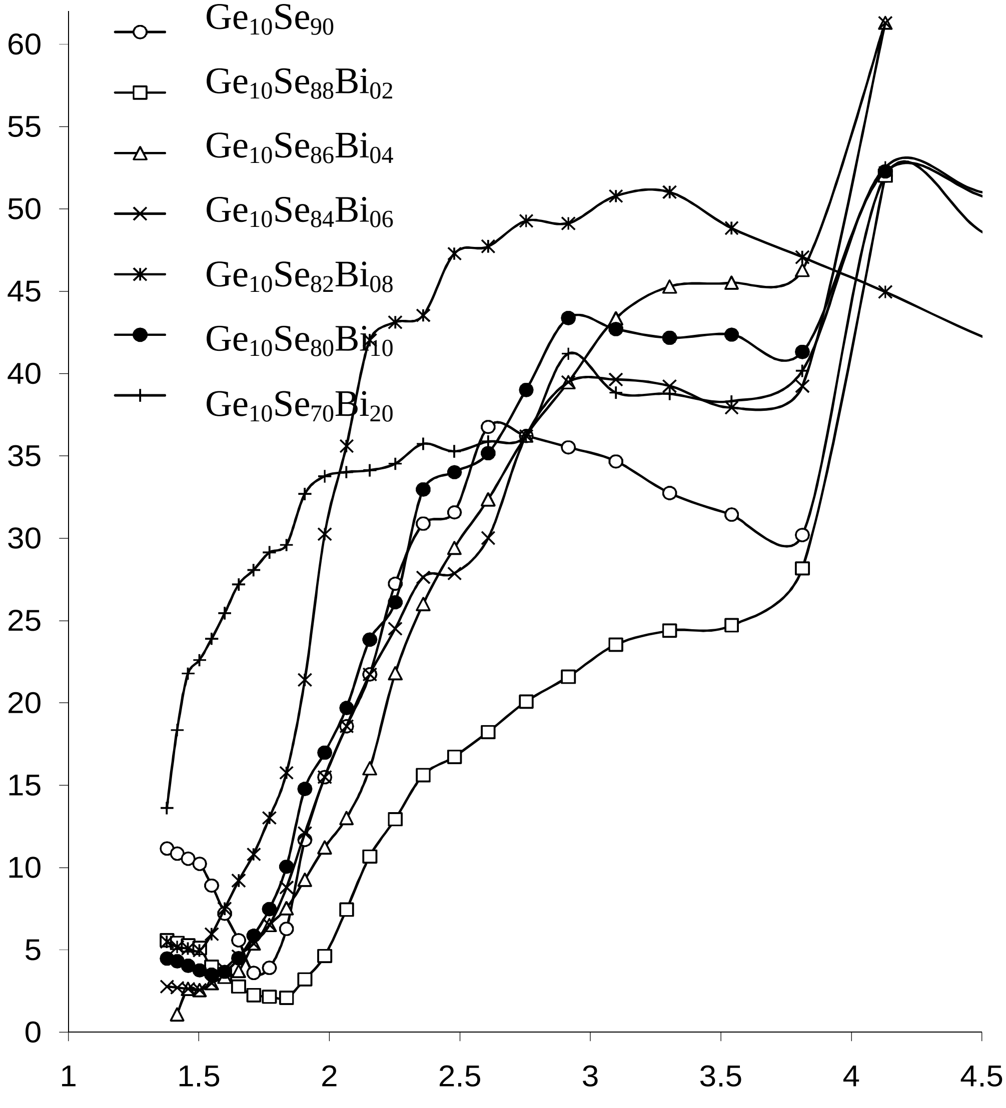

Fig. 3. Variation of Extinction coefficient (k) with photon energy in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^0C.

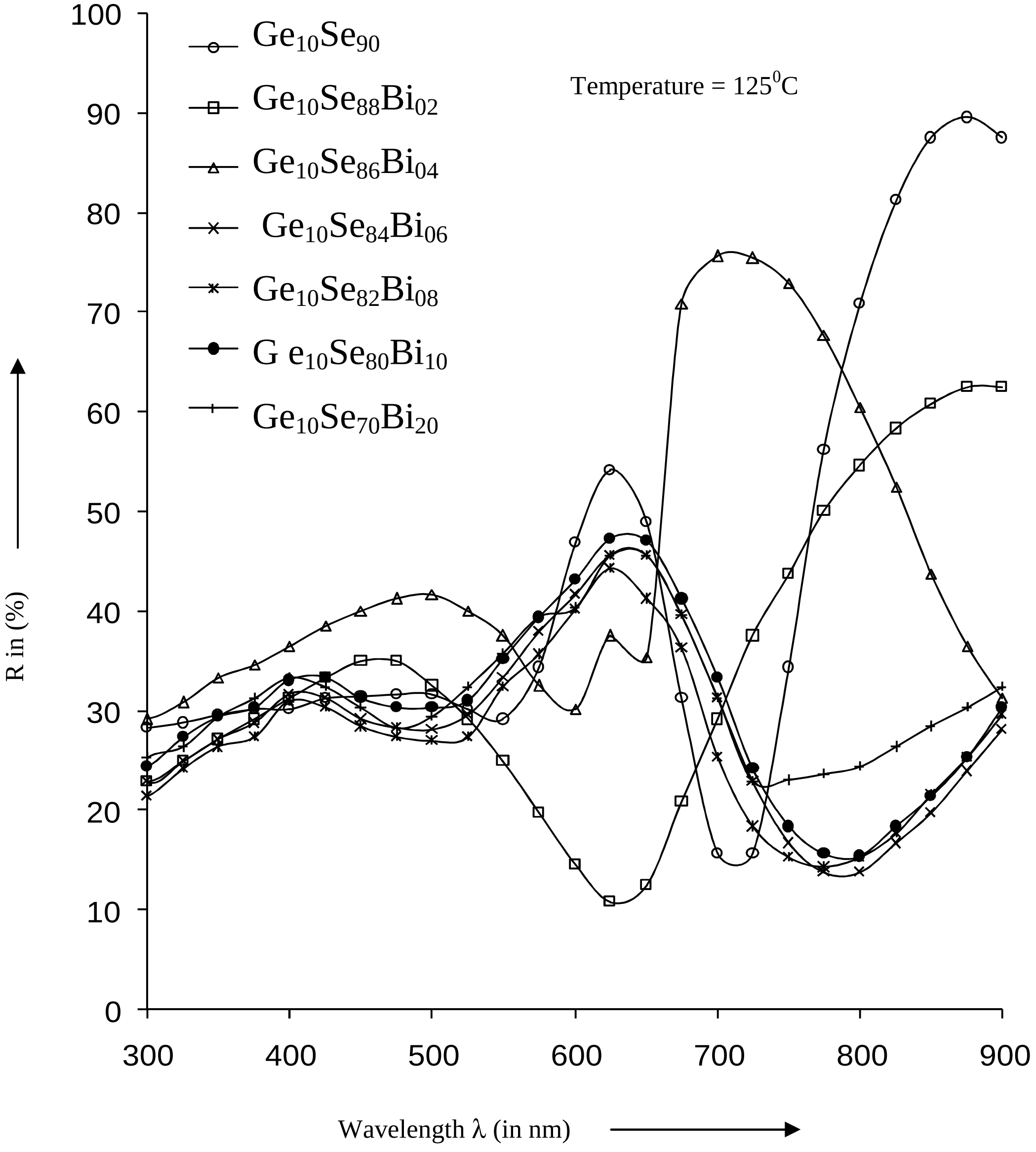

Fig. 4. Variation of Reflection (R) with wavelength in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^0C.

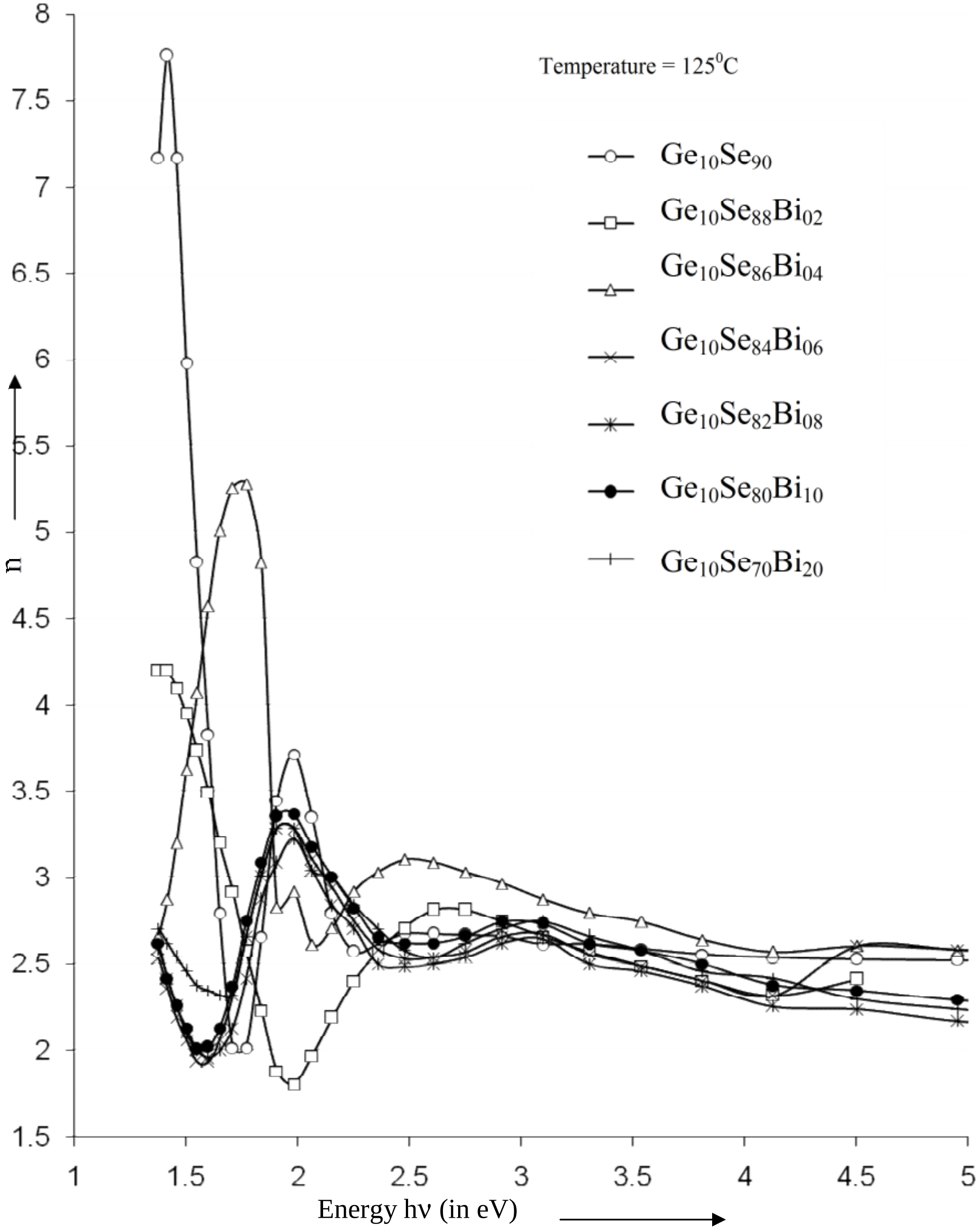

Fig. 5. Variation of Refractive Index (n) with photon energy in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^0C.

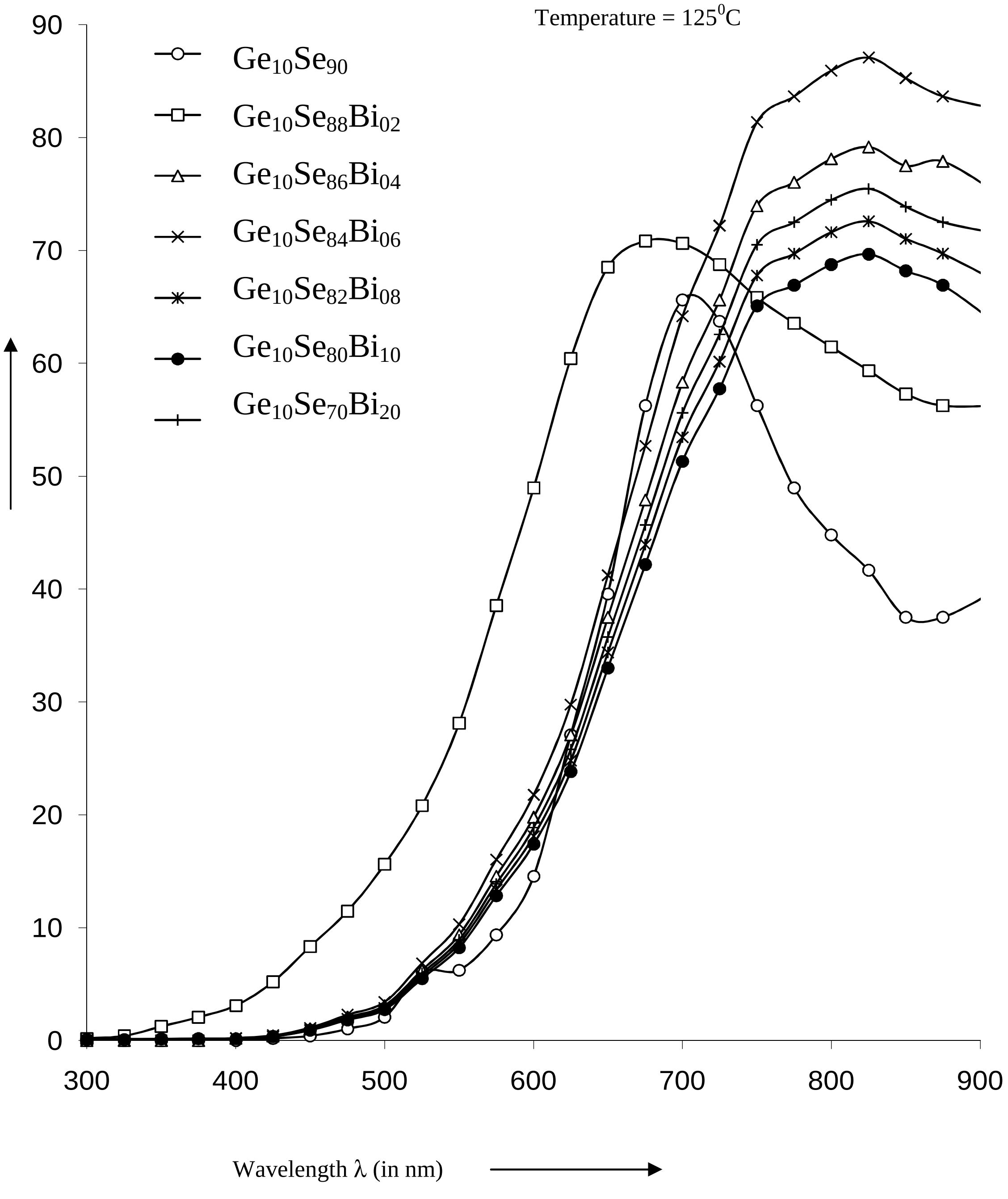

Fig. 6. Variation in Transmission (T) with Wavelength in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^{0}C.

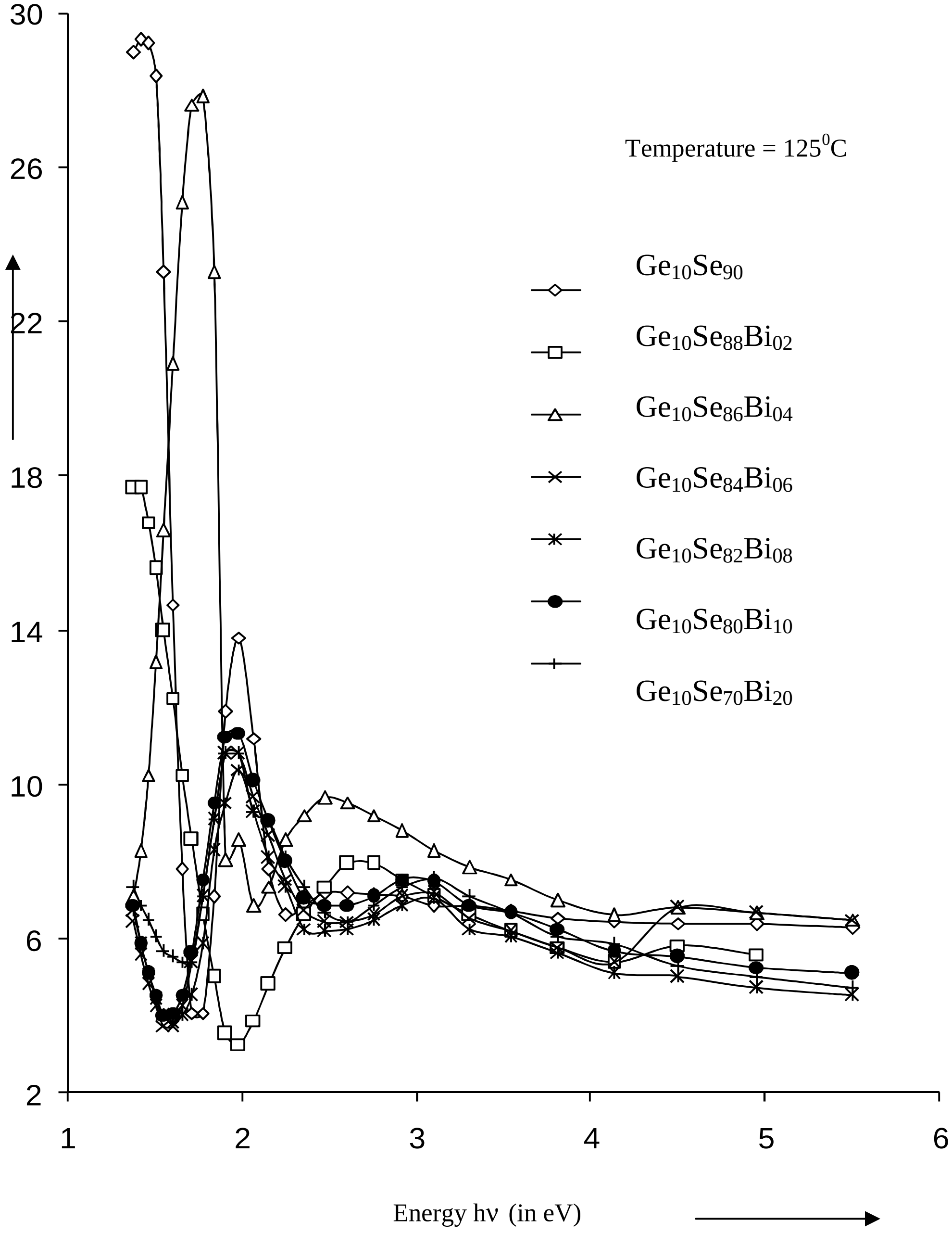

Fig. 7. Variation of Real part ($\in_r^{/} = n^2 - k^2$) of the dielectric constant with photon energy (hν) in a-$Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^0C.

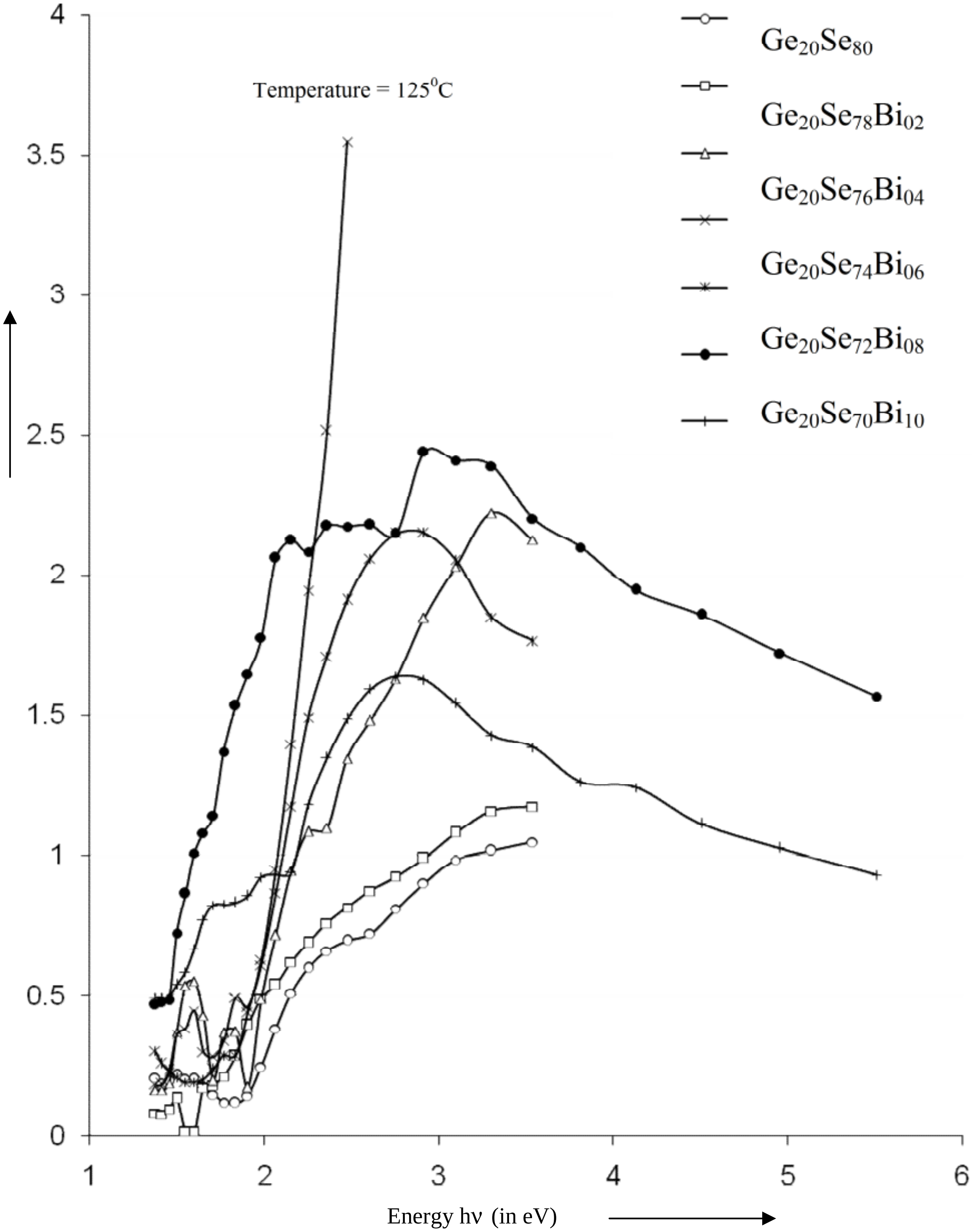

Fig. 8. Variation of Imaginary part ($\in_r^{//} = 2nk$) of the dielectric constant with photon energy (hν) in a-$Ge_{20}Se_{80-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films at Temperature 125^{0}C.

It may also due to the shift in Fermi level whose position is determined by the distribution of electrons over the localized states [32-33]. The values of the band gap are plotted in figure 17 for the batter understanding of the results.

In the last few decades particular attention has been devoted to the study of the physical properties of chalcogenide glasses in view of its possible application in photo electronic devices. Therefore much work has been done on both bulk and thin film samples of glassy chalcogenide regarding the optical properties [34-36]. The common feature of these glasses is the presence of localized states in the mobility gap as a result of the absence of long-range order as well as various inherent defects. The investigation of electron transport in disordered systems has gradually been developed and the investigation of gap states is of particular interest because of their effect on the electrical properties of semiconductors [37-38]. An increase in optical energy gap E_g after annealing at temperature below the glass transition temperature was observed in chalcogenide films [39-40]. The increase in E_g is attributed to the decrease in the density of tail states adjacent to the band edges [41-42]. The value of E_g of as deposited chalcogenide film was found to increase with the film thickness [43- 46]. It has been pointed out, in the Cu Ge-Te system that the bulk glass formation is centered on 20 at % of Ge. Homogeneous glasses could be obtained by progressively replacing Te by Cu up to 10% [38]. Ligero *et al.* [47] proposed that, the addition of copper to Ge-Te glasses system increases the crystallization ability and decreases the forming of Ge-Te glasses system. On the other hand, Barisova [48] suggested as Cu or Ge content increased in Cu-Ge-Te glasses, a progressive replacement of weak vonderWaals bonds which strengthening the glass structure. Ramesh et al. [49] studied the crystallization process of $Cu_x\ Ge_{15}\ Te_{85-x}$ glasses. These glasses exhibit a single crystallization stage. Vazquez *et al.* [50] reported the glass formation and diversification of alloys in the Cu-Ge-Te system by differential scanning calorimeter. They presented a comparison of various simple quantitative methods to asses the level of stability of the glassy materials in the above mentioned system. All of these methods are based on characteristic temperatures such as the glass transition temperature T_g, the onset temperature of crystallization T_{in}, the temperature corresponding to the maximum crystallization rate, T_p or melting temperature Tm. Electrical resistivity measurements tender pressures at ambient and low temperatures have been carried out on bulk, melt quenched $Cu_x\ Ge_{15}\ Te_{85-x}$ glasses ($2 < x < 10$) by Ramesh *et al.* [43]. They found that the resistivity's of these samples decrease continuously with pressure. From the above it is clear that very little attention is paid to optical properties of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) system. Optical properties of Ge_x,Se_{1-x} thin films have been studied most extensively [44 - 46]. When tellurium atoms are used instead of selenium, most of the observations are not valid. Thus it appears that Te atoms exhibit typical properties. Here we deal with new results associated with the special features of spectral characteristics of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films. The present work is mainly concerned with some experimental observations on the effect of heat treatment on the optical constants of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20).

Amorphous $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) thin films deposited by thermal evaporation were annealed at 125^0C temperatures which is below their crystallization temperatures for two hours. The optical band gap has been studied at room temperature and annealed films as a function of photon energy in the wavelength range (400 - 900 nm). It has been found that the optical band gap decreases with increasing annealing temperatures and increases on Bi concentration in the present system. It has been found that refractive index (n) and the extinction coefficient (k) increases on incorporation of Bi in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) system.

Fig. 1 shows the absorption coefficient (α) as a function of incident photon energy ($h\nu$) after annealing at 125^0C temperature. It has been observed that the value of absorption coefficient (α) increases exponentially with the increase in photon energy for different samples. It has also been observed that the value of absorption coefficient (α) increases with the increase in photon energy for at different sample films. In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to one of the three process firstly residual below-gap absorption, secondly Urbach tails and thirdly interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions and only the observable absorption with a gap under equilibrium conditions account for the first process. In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation. In crystalline materials the fundamental edge is directly related to the conduction and valance band, i.e. direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is observed. In these materials, α increases exponentially with the photon energy near the energy gap.

In various absorption processes, the electrons and the holes absorb both a photon and a phonon. The photon supplies the needed energy, while the phonon supplies the required momentum.

The value of indirect optical band gap (E_g) has been calculated from the plot of $(\alpha.h\nu)^{1/2}$ versus photon energy (hν) by taking the intercept on the X-axis to zero absorption with the photon energy. The variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) for room temperature and annealed films of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) system in Fig. 2.

The variation of the extinction coefficient (k), reflectance (R), refractive index (n), transmittance coefficient (T), real (ε'_r) and imaginary part (ε''_r) of the dielectric constants with photon energy and wavelength are plotted at room temperature and after annealing in Fig. 3-8.

The calculated values of E_g for the glassy samples of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) at annealed temperature are given in Table -1. It is evident from this table and figures that the value of optical band gap decreases with increasing annealing temperature and increases on Bi concentration. The increase in the optical band gap with increasing Bi concentration may be again be due to increase in grain size, the reduction in the disorder and decrease in density of defect states, which results in the reduction of tailing of bands. And also 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. Bismuth enters into the tetrahedral structure$GeSe_2$ forming units containing all the three elements (Ge, Se, Bi) leading to the modification of the glassy network. Further the optical band gap is strongly dependent on the fractional concentration of atoms.

Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap. During thermal annealing at temperature below the crystallization temperature, the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure consequently increasing the optical band gap. The decrease in the optical band gap is qualitatively in agreement with the concept that decreasing ionic character of the covalent bond lead to a small energy gap of the corresponding material of the system. The lone pair electrons adjacent to Bi atoms will have higher energies than those remote from Bi atoms causing a broadening and tailing of the lone pair valence band of the chacogen. This effect can account for the shallower slope with increasing Bi content. The slope of the curves $(\alpha\, h\nu)^{1/2}$ and $(\alpha\, h\nu)^2$ vs hν gives the β which is a measure of the structure randomness .The increase in the value of β with increase in the Bi content indicates the increase in the rigidity of the network and thus the modification in the network structure of the$Ge_{10}Se_{90}$ system. In extinction coefficient k curve shows a singe broad peak for lower Bi content and another peak starts appearing with increasing Bi content and peak position shift towards lower energy with increasing Bi content.

IV. CONCLUSION

From the above results and discussion, it may be concluded that the optical band gap increases up to 2 % of Bi concentration in $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) with further increase of Bi content the optical band gap decreases in the present system. The increase in the optical band gap with increasing Bi content may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands). The values of optical band gap (E_g) decrease at higher Bi concentration. Since the optical absorption depends on the short-range order in the amorphous state and defects associated with it. The decrease in the optical band gap in the present system may be due to reduction in the amount of disorder in the system and increase in the density of defects state. It may also due to the shift in Fermi level whose position is determined by the distribution of electrons over the localized states. This decrease in the optical band gap may be due to a decrease in the amount of disorder in the materials and an increase in the density of defect states. From the reflectance and transmittance studies of the thin films of $Ge_{10}Se_{90-x}Bi_x$ (where x = 0, 2, 4, 6, 8, 10 and 20) it may be concluded that the refractive index n decreases, while the value of the extinction coefficient k increases with photon energy. The study of the optical properties of $Ge_{10}Se_{90-x}Bi_x$ thin amorphous films showed a distinct variation in the refractive index n, absorption coefficient α, and extinction coefficient k, and optical band gap with the variation of Bi content.

1. The decrease in optical band with increasing Bi content is also related to the increase of Bi-Se bonds and the decease of Se-Se bonds.

2. The optical edge was found to shift towards lower values of photon energy with increasing Bi content the reason could be shrinking of the energy gap.
3. The variation in the value of extinction coefficient k and refractive index n could be explained in terms of charges induced stoichiometry, crystalline size and internal strain of the glassy alloy due to the introduction of Bi.
4. The energy dependence of optical absorption coefficient α is characterized by (a) the value obtained for α vary fairly high (b) all the films exhibit too distinct absorption regions, a high energy threshold and low energy threshold possibly corresponding to the two absorption mechanisms.
5. Energy band gap value was found decrease 1.24 to 1.01 eV for $Ge_{10}Se_{90-x}Bi_x$ at room temperature and 1.91 to 1.3 at anneling temperature with increasing Bi content (By Davis & Mott).
6. It was found that real (ε'_r) has two peaks and imaginary part (ε''_r) of dielectric constant shows a single broad peak but another peak starts appearing with increasing Bi content and becomes distinctly visible at higher Bi concentration. The lower energy peak in ε''_r spectrum corresponds to $\pi \rightarrow \sigma^*$ transitions while the higher energy p.

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