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Temperature Dependent and Optical Properties of Bi-Based Ge-Se Glasses

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Abstract : *Thermal diffusivity and optical band gap measurements on Bi doped germanium chalcogenides exhibit significant changes across the p→ n transition as a function of composition. The carrier type reversal,(CTR) which is purely an electronic property, should not, in principle, get manifested in thermal transport properties. The threshold maximum in thermal diffusivity which occur around 7 at. % of Bi content in* $Ge_{2o}Bi_xSe_{8o-x}$ *glasses is reported.*

Key Words : *Chalcogenide, Quenching Technique, Thermal Diffusivity*

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1. Introduction

The effect of impurities on the electronic properties of germanium chalcogenides have been a subject of great interest ever since their synthesis[1]. In recent years, a great deal of effort has been expended to understand the role of Bi in controlling the mechanism of electrical conduction in bulk chalcogenide glasses. It is known that bulk semiconducting glasses behave like intrinsic p-type semiconductors and are insensitive to impurity doping. Fermi level is considered to be pinned due to the equilibrium between the positively and negatively charged dangling bonds[2, 3]. But Bi doped germanium chalcogenides $Ge_{2o}Bi_xSe_{8o-x}$ show a carrier-type reversal (CTR) from p to n type at a certain doping level. This phenomenon of CTR was first observed in Ge-Bi-Se glasses[4, 5] and subtle changes around the critical Bi concentration, which is seen to occur in the vicinity of x = 7 at % in $Ge_{2o}Bi_xSe_{8o-x}$ glasses, have been reported. Their projected technological applications are in the manufacture of new class of p → n junctions[6] based entirely on glasses which offer many manufacturing advantages[7]. Electrical resistivity, thermoelectric power and optical absorption coefficient measurements on Ge-Bi-Se system by Tohge et al[8] shows a gradual decrease in resistivity with increasing Bi content up to 9 at. % and decreased by about four orders of magnitude between(x = 9 and 10)% but remain almost constant for x > 10 at. %. Composition dependence of Seebeck coefficient shows that glass containing 7.5 at. % of Bi is p-type, similar to other melt quenched chalcogenide glasses, but incorporation of more than 9 at. % of Bi changes it to n-type. They also report from optical band gap measurements that incorporation of 2.5 at.% of Bi into $Ge_{20}Se_{8O}$ glass results in decrease of Eg by as large as 0.65 eV, further addition of Bi causes only very small change in E_g and it is maintained constant for glasses containing more than 7.5 at.% of Bi. There are reports that heat capacity (C_p) measurements at 323K show a drastic change between x =6 and 8 at. %[9]. C_p, which is the difference between specific heats of glass and super cooled liquid, also show a maximum at 8 at. % of Bi. The d.c. electrical resistance measured on this sample shows an anomaly around x = 8 at. % of Bi[10]. In order to account for the observed variations in thermoelectric power, high pressure electrical resistivity etc. in Ge-Pb-Se glasses, which is another system exhibiting CTR and properties similar to the Ge-Bi-Se system, a structural model based on chemical nature of the constituents has been proposed[11] where the p -⟶ n transition has been attributed to the energetic disposition of the $Sp^3\ d^2$ band of Pb atoms, which is located closely above the lone pair band of Se. The CTR behavior observed in Bi containing chalcogenide glasses has also been accounted for by this model by these authors. Several mechanisms have been proposed to account for the influence of Bi doping in Ge-Se system. Analysis based on network modeling led Phillips[12] and Nagels et al[13] to conclude that CTR occurs in the vicinity of the percolation threshold and is the result of transport anomalies in the system. Studies of electrical, thermoelectric and optical properties as a function of composition led Tohge et al[8] to explain the transport mechanism on the basis of chemical bonds. Based on EXAFS data, Elliot and Steel[14] have discussed the reason for this mechanism as due to the formation of partially ionic Bi-chalcogen bonds and subsequent unpinning of the Fermi level. An alternate discussion by Storiopoulous and Fuhs[15] leads to the explanation that a drastic decrease in band gap induces an increase of conductivity and a reversal of conduction type. In all these models a chemically ordered network model is assumed for the glass structure in which formation of heteropolar bonds is favoured over homopolar bonds. Investigations on composition dependence of resistivity, heat capacity etc. are in accordance with the Phillips model where the assumptions made are that these glasses are inhomogeneous on the medium range scale and at a critical composition of the medium with p-type conduction, transition to n-type occurs. The purpose of the present work is to test whether any unusual feature is reflected in the composition dependence of optical and thermal properties of Bi doped Ge-Se glasses.

2. Experimental process:

Bulk semiconducting glasses with the general formula $Ge_{20}Bi_xSe_{80-x}$ ($0 < x < 12$) have been prepared in fused silica ampoules by the conventional melt-quenching technique. Starting with appropriate quantities of 5N purity elements. The cooling rate required to obtain uniform glasses from the melt is -200 K/s. The samples have been checked for vitreous nature by recording their X-ray powder diffraction spectra. The XRD patterns of typical samples prepared are shown in Fig.(1). The largest region of glass formation with bismuth was obtained for alloys with 20 to 30 at. % of Ge and 70 to 80 at. % of Se[8]. It is seen that for 20 at. % of Ge, the maximum bismuth content that can be incorporated into these glasses is 13 at. %, remaining being Se as shown in the phase diagram in Fig. (2). since these glasses have high crystallizing ability it is seen that further increase of bismuth gives partially crystallized glasses. Measurement of the thermal diffusivity of this system has been carried out using the PA phase lag technique. For measuring E, values using UV-Vis-NIR absorption method powdered samples have been used- Bulk glasses of diameter 5 mm and thickness.0.5 mm are used to carry out thermal diffusivity measurements.

3. Results and Discussions:

The optical absorption spectra recorded using UV-Vis-NIR absorption spectrophotometer [Hitachi Model U-3410] are shown in Figs. (3 and 4). The composition dependence of the optical band gap E_g is shown in Fig. (5). From this figure it is seen that the variations of E_g with the incorporation of more than 2 at. % of bismuth is very small and it remains constant for glasses containing more than 7 at. % of Bi. The addition of approximately 2 at. % of Bi into $Ge_{20}Se_{80}$ glass results in the decrease of Eg by 0.56 eV. This is in good agreement with the corresponding values reported by Tohge et al[8] where the addition of 2.5 at. % of Bi into $Ge_{20}Se_{80}$ glass result in the decrease of E_g by 0.65 eV.

The measured composition dependence of thermal diffusivity of $Ge_{20}Bi_xSe_{80-x}$ ($0 \leq x \leq 12$) glasses is shown in Fig (6). It is seen that a increases gradually with bismuth content up to 7 at. % of Bi, beyond which it decreases at a faster rate.. The optical band gap and thermal diffusivity values determined using UV-Vis-NIR spectrophotometer and photo acoustic technique respectively are tabulated in Table 1 along with the corresponding compositions. The mechanisms responsible for carrier type reversal and the peculiar variation in thermal conduction in these glasses can be explained in terms of the electronic and structural inhomogenity models respectively. In the electronic model, the various defect configuration of Bi are involved which brings about the unpinning of the Fermi level due to the perturbation of valence alteration pairs [VAPS] [16]. Structural inhomogenity model assumes the glass to be phase separated with n-type Bi-Se, submicroscopic entities embedded in the Ge-Se glass matrix [10]. Measurements on double stage crystallization give evidences for phase separation in these glasses[9].

Phillips and Thorpe have discussed in detail the features of the mechanical constraints theory in many of their papers[12, 17]. For binary glasses belonging to IV_x -$VI_{(loo-x)}$ group, they have predicted the critical composition to be around x = 20 at. % which corresponds to an average co-ordination number of Z = 2.4. Evaluation of Z for glasses, treating $Ge_{2o}Bi_xSe_{8o-x}$ this as a pseudo binary system, show that the value of x at which Z attains the critical value 2.4 is 7. However, for $Ge_xSe_{(l00-x)}$ glasses, this value is found to be at a slightly higher composition of X_c =23 at. %, which is attributed to the fact that not all bond bending constraints are effective in hindering intercluster motions [18]. There are reports that Bi_2Se_3, are n-type semiconductors[12, 19] and in glasses $Ge_{2o}Bi_xSe_{8o-x}$, the Bi_2Se_3, clusters are embedded in the Ge-Se glass matrix. The $Ge_{2o}Bi_xSe_{8o-x}$ glasses can be represented as $Ge_{20}Se_{80-5z}$ + Bi_zSe_{3z}. According to Phillips, when the Bi content is appreciably low, localized unconstructed Se defects are present in the Bi_2Se_3 tetradymite surfaces which are dispersed uniformly in the rest of $GeSe_2$ and Se flexible chains making them p-type semiconductors. At 6 at. % of Bi, the Bi_2Se_3 clusters retain in the melt. Also, x = 6 corresponds to $Ge_{2o}Se_{65}$-Bi_6Se_9 and $Ge_{20}Se_{65}$ = $Ge_{20}Se_{(100-y)}$ with y = 24 which agrees with the elastic stiffness threshold composition Y_c = 23 of the glasses found in other experiments[18]. At x 6 at. %, the Bi_2Se_3 tetradymite clusters find themselves in a matrix of increased mechanical rigidity and the mechanical misfit between the clusters become high which lead to a plastic deformation of these clusters. This give rise to an increase in Se defects which evolve in a percolative manner at the mechanical threshold and produce n-type conduction in these glasses. In terms of chemical bond formation, the carrier-type reversal from p-type to n-type is related to the formation of fairly large number of Bi-Se bonds and the disappearance of Se-Se bonds at this critical composition. According to the charged dangling bond model, the equilibrium between the positively and negatively charged dangling bonds which pins the Fermi level is affected maximum at this critical composition by charged impurities[4]. Vaidyanathan et al[11] have considered these glasses as a pseudo binary system with Bi acting as modifiers to the basic $Ge_{20}Se_{8O}$ network. The modification of the host network makes the Fermi level move towards the conduction band edge and alters the conduction mechanism from p-type to n-type. They have also proposed a structural model to explain the phenomenon of CTR. The dependence of thermal diffusivity a on Bi content of these glasses shows a threshold maximum around 7 at.% of Bi which lies very close to the value predicted by the constraints model. In the light of the earlier reports on phase separation in these glasses, the increase in a up to x = 7 can be attributed to the mechanical stiffening of Ge-Se network with the $BiSe_3$ clusters dispersed in it. The elastic misfit between the Bi_2Se_3 cluster and $GeSe_2$ network is relieved by distortions of the Se atom chains for x < 7. When x 7, the grown up Bi_2Se_3 cluster find themselves embedded in a matrix of increased mechanical rigidity. This enhanced elastic misfit leads to plastic deformation of Bi_2Se_3 clusters resulting in an increased density of Se defects. The finite frequency defect modes show up as fluctuations and internal surface modes in the rigid cluster regions. These cause a rapid decrease in thermal diffusion through the rigid network. Obviously, CTR being a purely electronic property should not get manifested in the thermal transport properties of the medium. However, the threshold maximum in a occurring at around 7 at.% of Bi content in $Ge_{2o}Bi_xSe_{8o-x}$ glasses can only be attributed to the effects due to the existence of a mechanical threshold at this composition. It so happens that the two occur at the same composition in Ge-Bi-Se glasses. Bismuth impurity induced structural modifications in the parent Ge-Se glass which is responsible for p n transition in these semiconductors is reflected in the optical absorption spectra[20]. Elliot and Steel [14] have suggested that the p→ n transition in these glasses is accompanied by a significant change in the local structural order surrounding the Bi impurity atoms. At low Bi concentrations, the Bi-Se bond remains covalent in character and at higher Bi concentrations it becomes partially ionic with slight increase in bond lengths[14]. It has further been proposed that the process of the dissolution of the Bi impurity in the selenium rich regions at lower concentrations produce Se centers making the Bi impurities positively charged. Further addition of Bi in larger concentrations does not produce appreciable additional defects as it enters in a modified network[14]. Consequently, the absorption edges are not appreciably affected. From the activation energy versus composition parameter data reported by Bhatia et al[21], at lower Bi concentrations there is little change in activation energy E_{av} whereas at higher concentrations a considerable decrease in E_{av} is observed which is explained as due to the shift in the Fermi level towards the conduction band. At present the origin of n-type conduction in Bi doped chalcogenide glasses is not fully understood. According to Nagels et al[13] the appearance of this conduction type in $Ge_{2o}Bi_xSe_{8o-x}$ glasses is assumed to be connected with the perturbation of the equilibrium of the negatively and positively charged dangling bonds induced by Bi as a charged impurity. The transition from p to n type with increasing Bi content is then related to the disappearance of Se-Se bonds. According to Tohge et al[8], in $Ge_{20}Se_{8O}$ glasses only Ge-Se and Se-Se bonds are supposed to be present. When Bi is incorporated into this glass, Bi is expected to combine freely with Se, followed by the decrease in the concentration of Se-Se bonds because the bond energy of Bi-Se bond is larger than that of the Bi-Ge bond (40.7 and 31 kcal/mole respectively)[22]. The concentration of Ge-Se bonds is almost constant over the whole composition range, whereas that of Bi-Se bond increases and that of Se-Se bond decreases monotonically with increasing Bi content up to 10 at.% after which the Se-Se bond vanishes. A further increase of the Bi content results in the formation of Bi-Bi or Bi-Ge bonds provided Bi is still six-fold co-ordinate with Se. Co-ordination numbers of four and two for Ge and Se respectively are assumed and the number of covalent bonds per Bi atom is reported to be six in these glasses[23]. Investigations on electrical properties on these glasses show an abrupt decrease in resistivity and the appearance of n-type conduction which is again related to the formation of fairly large number of Bi-Se bonds and the disappearance of Se-Se bonds. For six-fold co-ordinate Bi in crystalline Bi_2Se_3, the occurrence of sp^3d^3 or sp^3d^2 hybridization has been suggested. If this is the situation with Bi in chalcogenide glasses, the Bi-Se bond becomes electron deficient in the former case (or in the latter case) and Bi atom gets negatively charged which is compensated by the positive charge on the Se atom. Thus the equilibrium between the positively and negatively charged bonds which pins Fermi level is affected by the charged impurities which are described in the charged dangling bond model. Vaidyanathan et al[11] have proposed a structural model to explain the phenomenon of carrier type reversal in Pb doped germanium chalcogenides, which has then been extended to explain similar behaviour in Bi doped Ge-Se glasses. Spectroscopic investigations such as diffuse reflectance spectra and variation of optical energy gap obtained from peak maximum energies in DRS as a function of Pb concentration also show similar behaviour. FTIR spectra and Raman spectra together confirm that Ge and Pb or Bi in this type of glass system are present in tetrahedral and octahedral co-ordinations only using the above spectroscopic features. A structural model has been proposed on the basis of vibrational spectra and XANES. Thus Pb is assumed to be in a sp^3d^2 state of hybridization. The Se atoms are in sp^n (n= 1, 2 and 3) hybridization. Germanium utilizes its Sp^3 hybridized orbitals for bond formation. The lowest energy levels result from the overlap of the bonding orbitals. The Ge-Se and Ge-Ge bonds constitute the lowest energy levels. The next higher energy level is constituted of sp^n lone pair originating from Se. The sp^3d^2 orbitals of Pb ions are likely to occupy a slightly higher level and just above Se lone-pair levels. Similarly increase in Bi concentration in Ge-Bi-Se glasses leads to rapid growth of sp^3d^2 band and the top of sp band which results in the rapid increase of electron contribution to conductivity, which exceeds the contribution from holes. As a consequence p to n transition occurs as a function of Bi concentration. This overlap of orbitals with increasing Bi concentration brings about the decrease in E_g values. Only Pb and Bi containing Ge-Se glasses are known to exhibit such a p to n transition. This unique behaviour can be associated with the unique tendency of Bi towards octahedral co-ordination and more importantly with the energetic disposition of their d-bands which can overlap in energy with those of lone pair bonds of Se in particular. The closeness of the sp^3d^2 band with those of the lone pairs of chalcogen is suggested to be responsible in bringing about the carrier type reversal.

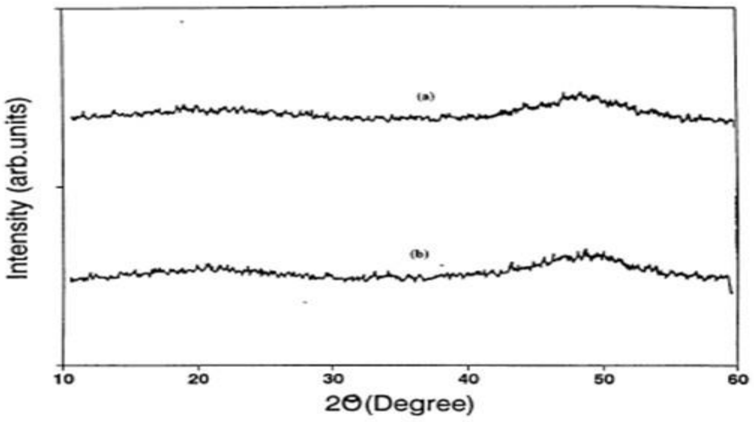

Fig. 1 X- ray diffraction pattern of (a)$Ge_{20}Bi_5Se_{75}$ and (b)$Ge_{20}Bi_{10}Se_{70}$ glasses.

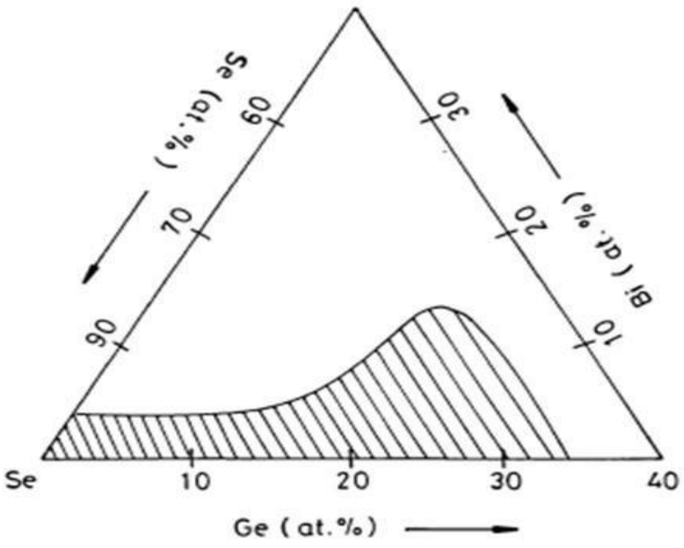

Fig. 2 Glass forming regions of Ge-Bi-Se system.

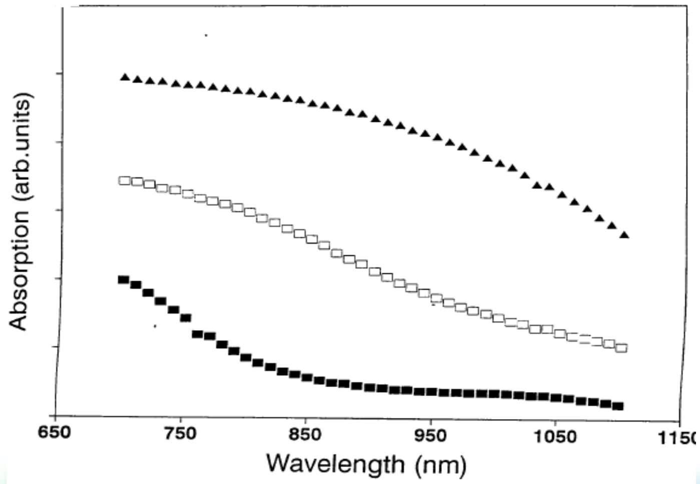

Fig. 3 UV-Vis - NIR spectra of $Ge_{20}Bi_xSe_{80-x}$ glasses.
(■) $Ge_{20}Bi_2Se_{78}$ (□)$Ge_{20}Bi_4Se_{76}$ (▲) $Ge_{20}Bi_7Se_{73}$.

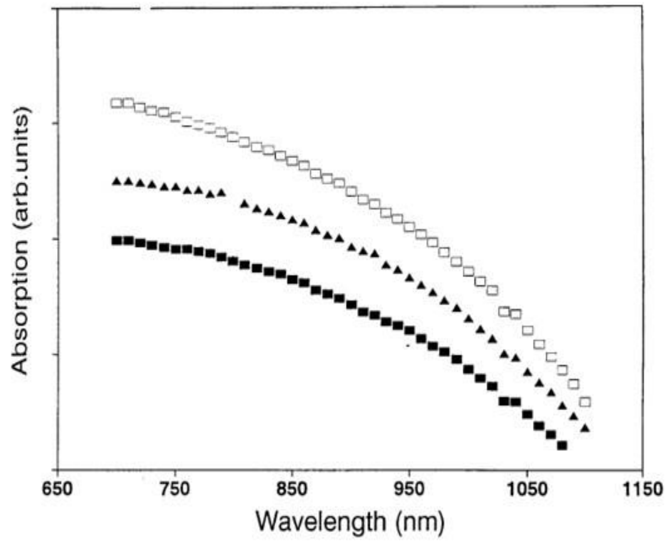

Fig. 4 UV-Vis - NIR spectra of $Ge_{20}Bi_xSe_{80-x}$ glasses.
(■)$Ge_{20}Bi_8Se_{72}$ (□) $Ge_{20}Bi_{10}Se_{70}$ (Δ)$Ge_{20}Bi_{12}Se_{68}$.

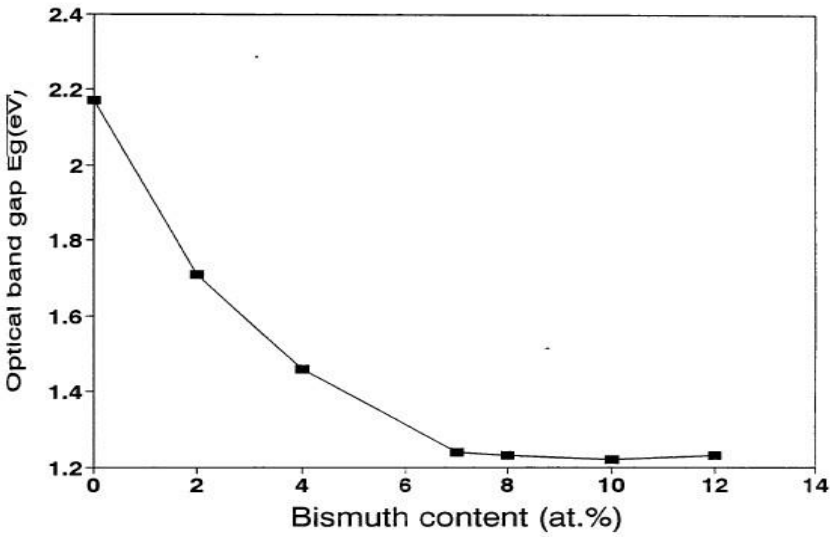

Fig. 5 Variation of the optical band gap Eg with average coordination number Z for the $Ge_{20}Bi_xSe_{80-x}$ glasses using UV-Vis-NIR absorption technique.

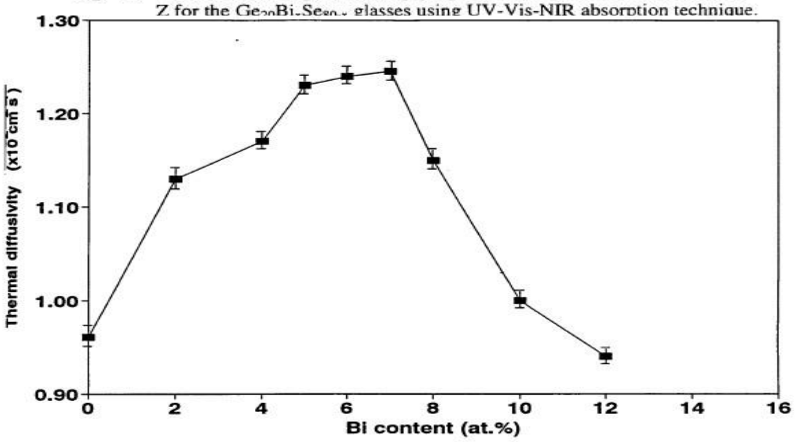

Fig. 6 Variation of thermal diffusivity α with average coordination number Z for $Ge_{20}Bi_xSe_{80-x}$ glasses.

Table 1

Composition dependence of thermal diffusivity α and energy gap E_g of Ge-Bi-Se glasses.

Composition			Z	α	E_g (eV)
Ge:	Bi:	Se		$(10^{-2}\ cm^2\ s^{-1})$	(UV-Vis-NIR method)
20	0	80	2.40	0.93	2.17
20	2	78	2.42	1.13	1.71
20	4	76	2.44	1.17	1.46
20	5	75	2.45	1.23	-
20	6	74	2.46	1.24	1.32
20	7	73	2.47	1.25	1.24
20	8	72	2.48	1.15	1.23
20	10	70	2.50	1.00	1.22
20	12	68	2.52	0.94	1.23

Conclusion

Thermal diffusivity and optical band gap measurements on Bi doped germanium chalcogenides using photo acoustic technique and UV-Vis-NIR absorption method respectively exhibit significant changes across the p→ n transition as a function of composition. The carrier type reversal, which is purely an electronic property should not, in principle, get manifested in thermal transport properties. The threshold maximum in thermal diffusivity which occur around 7 at.% of Bi content in $Ge_{2o}Bi_xSe_{8o-x}$ glasses can only be attributed to the effects due to the existence of a mechanical threshold in these glasses. The Eg data is in good agreement with the structural model proposed by Vaidyanathan et al[11]. It so happens that the two effects occur at the same composition. Whether any further correlation exists between mechanical rigidity and p → n type electronic transition need to be investigated with more experimentation and modeling.

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