4.1 Introduction

The effect of incorporation of Bi as an impurity in chalcogenide glasses has been a topic of great interest ever since the synthesis of such glassy systems. A great deal of effort has been expended to understand the role of Bi in controlling the mechanism of electrical conduction in chalcogenide glasses. Chalcogenide glasses are generally p-type semiconductors and are expected to be insensitive to the addition of impurities [1]. For them Fermi level is considered to be pinned due to the equilibrium between the positively and negatively charged dangling bonds which make them insensitive to impurity doping. But there are experimental results which are against this argument [2-5].

In the case of the Ge-Bi-Se system the addition of a critical quantity of Bi brings about a carrier type reversal from p-type to n-type in the basic Ge-Se system [6-8]. The Ge-Se system, which is a p-type semiconductor, changes to n-type with the addition of 7 atomic percent of Bi, which corresponds to an average coordination number $Z = 2.47$ for the system. Carrier type reversal has been observed in certain Pb doped germanium chalcogenides also [9]. Appreciable variations in different physical properties have been found around the composition with this critical Bi concentration, which occurs in the vicinity of $x = 7$ at.% (Coordination number $Z = 2.47$) in Ge-Bi-Se glasses with the general formula $\text{Ge}_{20}\text{Bi}_{x}\text{Se}_{80-x}$. 
Composition dependence of various physical properties such as thermoelectric power, electrical resistivity and IR absorption exhibit anomalies near the critical composition corresponding to \( x = 7 \) at.\%. Measurements by Tohge et.al [7] have shown a gradual decrease in resistivity with increasing Bi content up to 9 at.% and then decreases by about four orders of magnitude between \( x = 9 \) and 10 at.% but remain almost constant for \( x > 10 \) at %. Composition dependence of Seebeck coefficient shows that glass containing 7 at.% of Bi is p-type, similar to other melt quenched chalcogenide glasses but incorporation of 9 at.% of Bi changes it into n-type. In the case of optical band gap (\( E_g \)), a decrease by 0.65 eV was reported by incorporation of 2.5 at.% of Bi into Ge\(_{20}\)Se\(_{80}\) glass. Further addition of Bi causes only very small change in \( E_g \) and it remained constant for glasses containing more than 7.5 at.% of Bi. Heat capacity measurements at 323 K show a drastic change in the value of \( C_p \) between \( x = 6 \) and 8 at.%.

The carrier type reversal observed in Bi containing chalcogenide glasses has been accounted for by several authors. Studies of electrical, thermoelectric and optical properties as a function of composition led Tohge et.al [7-8] to explain the transport mechanism on the basis of chemical bonds. Based on EXAFs data, Elliot and Steel [10] have discussed the reasons for this mechanism as due to the formation of partially ionic Bi chalcogen bonds and subsequent unpinning of the Fermi level. Storiopoulous and Fuhs [11] have put forwarded the explanation that a drastic decrease in band gap induces an increase of conductivity and a reversal in the type of the carriers. Analysis based on network modeling led Phillips[8] and Nagels to conclude that carrier type reversal occurs in the vicinity of the percolation threshold and is the result of transport anomalies in the system.

In the present work our aim is the investigation of the composition dependence of photoconductivity and carrier lifetime in Ge\(_{20}\)Bi\(_x\)Se\(_{80}\)\(_x\) glasses with \( x \) varying 2 to 12 at.\%. The average coordination number (Z) of this system varies from 2.4 to 2.52 corresponding
to the above variation in $x$. Temperature dependence of photoconductivity has also been measured and analysed. The objective in this work is to test whether any special feature is reflected around the critical composition of Ge-Bi-Se glasses at which p-n transition has been reported.

4.2 Experimental method

Bulk semiconducting glasses with the general formula $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ ($0 < x < 12$) have been prepared by the conventional melt quenching technique starting with 5N purity constituents. The cooling rate is approximately $500^\circ$C/Sec. The amorphous nature of the samples have been checked by X-ray powder diffraction method. Two compositions have been analysed by XPS.

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\cite{7}. It is seen that for 20 at.\% of Ge, the maximum Bi content that can be incorporated into the glass matrix is 13 at.\%, the remaining being selenium. If bismuth content is increased further, the glasses formed may be partially crystallised. Measurements of photoconductivity and carrier lifetime have been carried out as has already been described in Chapter 2.

Bulk samples having rectangular shape with surface area $3 \times 4 \text{ mm}^2$ and thickness 0.5 mm have been prepared for the present measurements. The samples have been sandwiched between two SnO$_2$ coated conducting transparent glass plates for the measurements. The contacts have been found to be ohmic from V-I characteristic study. The sample has been illuminated by light from a Xe arc lamp. The intensity of light falling on the sample is 25 mWcm$^{-2}$ during photoconductivity and carrier lifetime measurements.
4.3 Results and discussion

4.3.1 Temperature, intensity and spectral dependence

Temperature dependence of dark conductivity for Ge$_{20}$Se$_{80}$, Ge$_{20}$Bi$_2$Se$_{78}$ and Ge$_{20}$Bi$_{10}$Se$_{70}$ are shown in Fig.4.1. The behaviour is almost identical to earlier reports [7-12]. Temperature dependence of a.c photoconductivity and d.c photoconductivity for the same compositions are shown in figures 4.2 and 4.3 respectively. In both these cases photoconductivity initially increases gradually with inverse temperature and then decreases. The same behaviour is exhibited by other compositions of the Ge-Bi-Se system. Photoconductivity increases by nearly two orders of magnitude with the addition of bismuth, as is clear from figures 4.2 and 4.3. The increase is reflected more or less identically in both a.c (pulsed excitation) and d.c (steady state) measurements. The enhancement in photoconductivity can be attributed to the increase in the density of charged defect states formed in the energy gap with the addition of bismuth[13].

![Figure 4.1](image-url)  
**Fig.4.1** Variation of darkconductivity with temperature (plotted as 1/T). ( ■ ■ ■ ■ ■ . . . . . Ge$_{20}$Se$_{80}$,  □ □ □ □ □ . . . . . Ge$_{20}$Bi$_2$Se$_{78}$, and ▲ ▲ ▲ ▲ ▲ ▲ . . . . . Ge$_{20}$Bi$_{10}$Se$_{70}$)
Fig. 4.2 Variation of a.c photoconductivity (plotted as $\log \sigma_{ph}$) with inverse temperature for three compositions of Ge-Bi-Se system. (Ge$_{20}$Se$_{80}$ .......■■■■, Ge$_{30}$Bi$_{10}$Se$_{70}$ ....... ▲▲▲ Ge$_{20}$Bi$_{2}$Se$_{78}$ .......□□□□). Chopping frequency is 20 Hz. Uncertainty in the values are less than 5%.

Fig. 4.3 Variation of d.c photoconductivity with inverse temperature for Ge$_{20}$Se$_{80}$ .......■■■■, Ge$_{30}$Bi$_{10}$Se$_{70}$ ....... ▲▲▲ and Ge$_{20}$Bi$_{2}$Se$_{78}$ .......□□□□.)
may be hopping conduction through the defect states. Another reason may be the change in band gap with the addition of bismuth. From Fig.4.4 it can be seen that the band gap decreases appreciably by the incorporation of 2 at.% and 4 at.% of bismuth. Further addition of bismuth does not alter the band gap appreciably. Therefore it can be concluded that the observed general increase in photoconductivity of Ge-Bi-Se system compared to Ge-Se is also related to the shrinkage of the band gap[4].

The variation of optical band gap together with that of activation energy for conduction is plotted in Fig.4.4. The activation energy does not change significantly for lower concentrations of bismuth. Similar results have been obtained by Tohge et.al.[7]. At low Bi concentrations the optical band gap decreases appreciably with increase of Bi content. At higher Bi concentrations optical band gap remains unaltered whereas activation energy decreases. This occurs as a result of the shift of the Fermi level towards

Fig.4.4 Variation of optical band gap (............ ■■■■■) and activation energy for conduction (.................+++++) with increase in Bi content.
the conduction band [14]. Fig.4.5 shows the variation of photoconductivity with intensity of incident light for the sample Ge$_{20}$Bi$_{10}$Se$_{70}$. Other compositions show similar variation. Photoconductivity exhibits almost a linear variation at lower intensities of illumination and become almost constant at higher intensities of illumination. The results shown in Fig.4.5 indicate that photoconductivity saturates at higher intensities of illumination.

![Graph showing variation of photoconductivity with intensity of illumination for Ge$_{20}$Bi$_{10}$Se$_{70}$ and Ge$_{20}$Bi$_{12}$Se$_{78}$ glasses. Other compositions have similar variations.](image)

**Fig.4.5** Variation of photoconductivity with intensity of illumination for Ge$_{20}$Bi$_{10}$Se$_{70}$ (□□□□□□□□) and Ge$_{20}$Bi$_{12}$Se$_{78}$ (■■■■■■■■) glasses. Other compositions have similar variations.

The results on photoconductivity of Ge-Bi-Se system have been analysed in terms of the ABFH model and the results are shown in Fig.4.6. In the frame work of ABFH model the material exhibits characteristics of a type I photoconductor. A plot of $E_g$ vs $T_m \ln(\sigma_{max})$ is shown in Fig.4.6. The points obtained can be fitted to a straight line. Referring to the description of the ABFH model based analysis for our photoconductivity data on these glasses fit very well with that of a type I photoconductor.
Fig. 4.6 Plot of $E_g$ against the product $T_m \ln \sigma_{max}$ for the Ge$_{20}$Bi$_x$Se$_{80-x}$ system. The points can be fitted to a straight line.

The spectral dependence of photoconductivity for Ge$_{20}$Se$_{80}$ and Ge$_{20}$Bi$_2$Se$_{78}$ have been measured and are plotted in Fig. 4.7. The photocurrent is normalised for the intensity.

Fig. 4.7 Spectral dependence of photoconductivity in Ge$_{20}$Se$_{80}$ and Ge$_{30}$Bi$_2$Se$_{78}$. 
variation of the source and normalised photoconductivity gives actually quantum efficiency of the sample. Though the normalised photocurrent peaks around the absorption edge, a correct determination of the band gap is not possible from the data obtained. In general, the quantum efficiency of Ge-Bi-Se system is found to be less than that of Ge-In-Se by nearly two orders of magnitude.

4.3.2 Frequency resolved photoconductivity (FRPC) measurements.

FRPC measurements have been carried out on different compositions of $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system and the plots for four compositions are shown in Fig. 4.8. Also FRPC measurements have been carried out on various compositions at different temperatures and intensities of illumination. Each curve is normalised with respect to its maximum value. The peak position shifts to higher frequencies with increase of temperature or intensity for all the compositions. The frequency ($f_{\text{max}}$) corresponding to the peak in

![Graph showing FRPC measurements in four compositions of the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system.](image)

Fig. 4.8 FRPC measurements in four compositions of the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system. (■ ... $x = 2$, ++++ ... $x = 6$, ** ** ....... $x = 8$, □ □ ... $x = 12$)
photoconductivity, is noted from the figures and the carrier lifetime ($\tau$) is determined. The carrier lifetime is calculated from the formula $\tau = \frac{1}{2\pi f_{\text{max}}}$. It is found to possess an almost linear variation with temperature as shown in Fig. 4.9. Since the carrier lifetime exhibits a linear decrease with temperature we can assume that the number of traps in the band gap increases with temperature. Similar results have been reported for other chalcogenides by earlier workers\[15\]. The carrier lifetime measured by FRPC method is found to decrease almost exponentially with intensity. At high intensities there is no appreciable decrease and the carrier lifetime almost constant. The plot of carrier lifetime vs intensity for the composition $\text{Ge}_{20}\text{Bi}_{2}\text{Se}_{78}$ obtained by FRPC measurement is shown in Fig. 4.10. Carrier lifetime ($\tau$) and generation rate $G$ are related as $\tau = AG^v$. From $\ln G$ vs

![Graph](image_url)

**Fig. 4.9** Temperature dependent variation of carrier lifetime measured by FRPC method for $\text{Ge}_{20}\text{Bi}_{2}\text{Se}_{78}$ (..■■■..) and $\text{Ge}_{30}\text{Bi}_{10}\text{Se}_{70}$ (..□□□..) samples
In the \( \ln \tau \) plot the value of the exponent \( \nu \) can be obtained. Generation rate, \( G \) is directly proportional to the intensity of illumination. From the plot shown in Fig. 4.11 the value of the exponent \( \nu \) have been calculated for Ge\(_{20}\)Bi\(_2\)Se\(_{78}\) and Ge\(_{30}\)Bi\(_{10}\)Se\(_{70}\). The value of \( \nu \) for these are \( \approx 0.62 \) and \( \approx 0.867 \). For other compositions also similar calculations have been done and for all of them the value of the exponent \( \nu \) lies between 1 and 0.5 which is an indication for the presence of localized states in the band gap of the material as explained with the results of Ge-In-Se\([16-20]\). Composition dependent variation of carrier lifetime is shown in Fig. 4.12. In general carrier lifetime decrease with increase in Bi content. It exhibits a clear slope change corresponding to the critical composition where \( p \rightarrow n \) transition has been reported by earlier workers. A discussion of composition dependent behaviour of Ge-Bi-Se system is given in the next section where the explanations by different workers are outlined.
Fig. 4.11 Plot of \( \ln G \) vs \( \ln \tau \) for \( Ge_{20}Bi_{15}Se_{78} \) and \( Ge_{30}Bi_{10}Se_{70} \).

Fig. 4.12 Variation of carrier lifetime with Bi content. The measurements have been carried out at 298 K. Intensity of light 25 mWcm\(^{-2}\).
4.3.3 Composition dependence of photoconductivity

The composition dependence of photoconductivity ($\sigma_{ph}$) is shown in Fig.4.13 and that of photodetectivity, the ratio of photoconductivity to dark conductivity ($\sigma_{ph}/\sigma_d$), is shown in Fig.4.14. Both $\sigma_{ph}$ and $\sigma_{ph}/\sigma_d$ have sharp variations around the critical composition $x=7$ corresponding to $Z=2.47$ where the $p\rightarrow n$ transition occurs. In general, photoconductivity increases upto $x=6$ and then decreases to a minimum and thereafter remain more or less constant. But photodetectivity, in general, decreases with increase in $x$ and it remains almost constant beyond $x=7$. Photodetectivity (or photosensitivity) of the material is a factor which determines the quality of a photoconductor in using it as a photodetector.

Although $p\rightarrow n$ transition and anomalous change of many physical properties have been analysed and explained by various authors before [6-8, 20-22], the mechanism of this phenomenon is not yet fully understood. More experimentation and modeling seem to be necessary to get a clear picture of the mechanisms involved in the process. Studies of electrical, thermoelectric and optical properties as a function of composition led Tohge et.al[6] to explain the transport mechanism in Ge-Bi-Se glasses on the basis of chemical bonds. Based on EXAFs data Elliot and Steel [9] have attributed the mechanism to the formation of partially ionic Bi-chalcogen bonds and the subsequent unpinning of the Fermi level. They suggested that the $p\rightarrow n$ 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 bonds remain covalent in character and at higher Bi concentrations, it becomes partially ionic with a slight increase in bond length[9]. 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 don't produce appreciable additional defects as it enters a modified network. Consequently the absorption edges are not appreciably affected.
Chapter 4

Ge-Bi-Se glasses

Fig. 4.13 Variation of photoconductivity with increase in Bi content in the Ge-Bi-Se system.

Fig. 4.14 Variation of photodetectivity with increase in Bi content.
Phillips[8] and Thorpe [23] predicted the critical composition of the binary glass system of the type $IV_x\cdot V_{100-x}$ to be around $x= 20$ at.% which corresponds to average coordination number $Z= 2.4$, IV and VI indicating the corresponding group of elements in the periodic table. According to this we can expect a critical composition for the $Ge_{20}Bi_xSe_{80-x}$ system to be around $x=7$ at.%. However, for $Ge_xSe_{100-x}$ glasses, this value is found to be slightly higher, at $x=23$ at.%, which is attributed to the fact that not all bond bending constraints are effective in hindering inter cluster motions[24]. There are reports that Bi$_2$Se$_3$ is an n-type semiconductor and in Ge-Bi-Se glasses the Bi$_2$Se$_3$ clusters are embedded in the Ge-Se glass matrix[8, 25]. The $Ge_{20}Bi_xSe_{80-x}$ glasses can be represented as $Ge_{20}Se_{80-y}+ Bi_{2}Se_{y}$. According to Phillips, when Bi content is appreciably low localized unconstrained Se$^{-}$ defects are present in the Bi$_2$Se$_3$ 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$_2$Se$_3$ clusters retain in the melt. Also $x=6$ corresponds to $Ge_{20}Se_{65}Bi_{6}Se_{9}$ 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 binary glasses found in other experiments[24]. At $x>6$ at.% the Bi$_2$Se$_3$ 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 gives 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 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 charge dangling bond model, the equilibrium between the positively and negatively charged dangling bonds which pin the Fermi level is affected maximum at this critical composition by charged impurities[7].

Bhatia et.al [21] have reported that, at lower Bi concentrations there is little change in the 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. According to Tohge et al. [7], in Ge_{20}Se_{80} 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 the Bi-Se bond is larger than that of a Bi-Ge bond (40.7 and 31 k cal/mole respectively) [26]. The concentration of Ge-Se bonds remain the same 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 coordinated with Se. Coordination numbers four and two are assumed for Ge and Se respectively and the number of covalent bonds per Bi atom is reported to be six in these glasses [27]. Investigations on electrical properties on these glasses show an abrupt decrease in resistivity which may be related to the formation of fairly large number of Bi-Se bonds and the disappearance of Se-Se bonds. For six fold coordinated Bi in crystalline Bi_{2}Se_{3}, the occurrence of p^{3}d^{3} or sp^{3}d^{2} hybridisation have been suggested. If this is the situation with Bi in chalcogenide glasses, the Bi-Se bond becomes electron deficient and Bi atoms get negatively charged which is compensated by the positive charge on the Se atoms. Thus the equilibrium between the positively and negatively charged bonds which pins the Fermi level are affected by the charged impurities which is described in the charged dangling model. Sunil Kumar et al. [28], based on XPS measurements of Ge-Bi-Se thin films have suggested that Bi atoms are positively charged. According to their results, the charged Bi atoms perturb the equilibrium between positively and negatively charged defect centers, thereby causing a shift of the Fermi level towards the conduction band.

Vaidyanathan et al. [29] have considered the Bi based glasses as a pseudobinary system with Bi acting as network modifiers to the basic Ge_{20}Se_{80} 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 carrier type reversal in Pb incorporated
germanium chalcogenides. Spectroscopic investigations such as diffuse reflectance spectra and variation of optical energy gap obtained from peak maximum energies in diffuse reflectance spectra as a function of Pb concentration also show similar behaviour. FTIR and Raman spectra together confirm that Ge and Pb or Bi in this type of glass system are present only in tetrahedral and octahedral coordinations using the above spectroscopic features.

The Pb is assumed to be in a \( \text{sp}^3 \text{d}^2 \) state of hybridisation. The Se atoms are in \( \text{sp}^n \) \((n=1, 2, \text{ and } 3)\) hybridisation. Germanium utilises its \( \text{sp}^3 \) hybridised 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 by \( \text{sp}^n \) lone pair originating from Se. The \( \text{sp}^3 \text{d}^2 \) 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 a rapid growth of \( \text{sp}^3 \text{d}^2 \) band which results in the rapid increase of electron contribution to conductivity which exceeds contribution from holes. As consequence \( p \rightarrow n \) transition occurs as a function of Bi concentration. Only Pb and Bi containing Ge-Se glasses are known to exhibit such a \( p \rightarrow n \) transition. Bi and Pb have a unique tendency towards octahedral coordination and more importantly the energetic disposition of their d-bands, which can overlap in energy with those of lone pair bonds of Se, in particular, may be the reasons for this \( p \rightarrow n \) transition.

Based on the various explanations, we can draw the following general conclusions regarding photoconductivity of Ge-Bi-se glasses. The Ge-Bi-Se system is a pseudo binary system with Bi atoms acting as an impurity. The Bi atoms modify the structure of the host Ge-Se network and it results in the shifting of the Fermi level towards the conduction band. The decrease in photoconductivity beyond \( x=6 \) \((Z=2.46)\) at.\% can be explained as due to the formation of Bi\(_2\)Se\(_3\) ionic bonds and the corresponding disappearance of Se-Se bonds. In the interpretation given by Vaidyanathan et.al [29], the disappearance of Se-Se bonds with increase in Bi content is outlined as due to the overlap of d-orbitals of Bi or Pb
with those of lone pair bonds in Se. The increase in defect concentration due to the addition of bismuth may be the reason for the decrease in carrier lifetime with increase in Bi content. Carrier lifetime decreases in general with increase of Bi content and exhibits a clear slope change around the critical composition with x=7 as shown in Fig.4.12. At the same time photoconductivity slightly increases with increase in Bi content and around the critical composition it exhibits a rise and a clear decrease as shown in Fig.4.13. It is interesting to note that the average coordination(Z) of this composition is 2.47 close to which the system has a mechanical threshold according to Phillips-Thorpe model.

4.4 XPS analysis of Ge-Bi-Se glasses

Two compositions from the Ge\textsubscript{20}Bi\textsubscript{x}Se\textsubscript{80-x} system, namely with x=2 and x=10 have been analysed by x-ray photoelectron spectroscopy. The composition with x=2 is p-type while that with x=10 is n-type. The binding energy values of the characteristic levels of pure Ge,Bi and Se as well as their values in the two compositions obtained from XPS spectra are show in Table 4.1. The corresponding spectra are given in figures 4.15, 4.16 and 4.17.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ge 3P\textsubscript{3/2}</th>
<th>Bi 4f\textsubscript{7/2}</th>
<th>Se 3P\textsubscript{3/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure element</td>
<td>120.8</td>
<td>157.4</td>
<td>161.9</td>
</tr>
<tr>
<td>Ge\textsubscript{20}Bi\textsubscript{2}Se\textsubscript{78} (Z=2.42)</td>
<td>121.7 (+0.9)</td>
<td>158.5 (+1.1)</td>
<td>161.2 (-0.7)</td>
</tr>
<tr>
<td>Ge\textsubscript{20}Bi\textsubscript{10}Se\textsubscript{70} (Z=2.5)</td>
<td>121.3 (+0.5)</td>
<td>158.6 (+1.2)</td>
<td>160.8 (-1.1)</td>
</tr>
</tbody>
</table>
Fig. 4.15 XPS of 3p\textsubscript{3/2} levels of pure germanium (A), germanium in Ge\textsubscript{20}Bi\textsubscript{5}Se\textsubscript{78} (B) and in Ge\textsubscript{20}Bi\textsubscript{10}Se\textsubscript{70} (C).

Fig. 4.16 XPS of 4f\textsubscript{7/2} levels of pure Bi (A), Bi in Ge\textsubscript{20}Bi\textsubscript{5}Se\textsubscript{78} (B) and in Ge\textsubscript{20}Bi\textsubscript{10}Se\textsubscript{70} (C).
As is clear from the figures, Bi suffers a positive shift in its 4f level for the two compositions compared to that of the pure element. Germanium also undergoes positive shift when the compound is formed. But the b.e values of selenium is found to decrease in the compounds compared to that of pure selenium. The shifts can be attributed to the bonds formed and variation in number of structural units in the two compositions. The differences in electronegativity values could also be responsible for the observed shifts.

**4.5 Conclusions**

Our investigations indicate that photoconducting properties of Ge-Se system in general improves by the incorporation of Bi. The increase is nearly of the order of two. Photoconductivity exhibits a clear change corresponding to the critical composition of the Ge-Bi-Se system at which the material undergoes a p→n transition. At the same time
photodetectivity($\sigma_{ph}/\sigma_d$), in general, decreases with the incorporation of bismuth. Photodetectivity also exhibits a clear change at the critical composition. Carrier lifetime measured by FRPC method, decreases in general with the incorporation of bismuth. Carrier lifetime has a sharp slope change around the critical composition. These results are analysed in the light of various models and explanations proposed by different research workers. Analysis of the material in terms of ABFH model reveals that the Ge-Bi-Se system is a TypeI photoconductor. One n-type and one p-type compositions have been analysed by XPS and the results are discussed.
4.6 References

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