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Photoconductivity and carrier lifetime in In/Bi doped Ge–Se glasses

G Mathew and J Philip

Department of Instrumentation, Cochin University of Science and Technology, Cochin 682 022, India

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Abstract. Photoconducting properties of the $\text{Ge}_x\text{Se}_{100-x}$ bulk semiconducting glass system are found to improve with the addition of indium or bismuth. In the $\text{Ge}_x\text{In}_5\text{Se}_{95-x}$ system, appreciable variations in photoconductivity and carrier lifetime are found to occur at average atomic coordination numbers $Z = 2.41$ and 2.73 . These are explained on the basis of the mechanical threshold and chemically ordered covalent network (COCN) models. In the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system, a sharp decrease in photoconductivity and carrier lifetime are observed at the composition corresponding to $x = 7$ ($Z = 2.47$), where a p-type to n-type transition has been reported earlier. Although differences in many of their properties do exist, Ge–Se, Ge–In–Se and Ge–Bi–Se systems remain type I photoconductors and their behaviour can be analysed in terms of the ABFH model.

1. Introduction

The electrical properties of chalcogenide glasses are not, in general, affected appreciably by the incorporation of impurities because the random network of atoms can accommodate an impurity without creating an extra electron or hole. This concept is based on the fact that an impurity atom can satisfy its valence requirements by adjusting its nearest neighbour environment, thus causing negligible effect on the electrical properties [1]. Another argument is that the high density of localized states present in the forbidden gap effectively pins the Fermi level. However, experimental results reported by various authors have shown that there are selected cases in which addition of impurity atoms does change the electrical properties of chalcogenide glasses significantly [2–5]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Impurity concentration obviously is a critical factor in such cases because all impurities cannot behave in an electrically active manner. Several of the physical properties are found to improve by the addition of certain impurities. Therefore, investigations on the influence of impurities on the properties of chalcogenide glasses are of relevance both from basic science and application point of view.

In this paper we present the results of our work on the photoconducting properties of two ternary chalcogenide glass systems, namely Ge–In–Se and Ge–Bi–Se. These two systems can be considered as consisting of the basic Ge–Se network with appropriate amounts of In or Bi added as impurities. The glass forming region of the Ge–In–Se system includes compositions with average coordination numbers (Z) ranging from 2.39 to 2.79. It is an ideal system to investigate on account of the fact that it is possible to isolate the effects of chemical origin from those of structural origin. The above composition range contains two mechanical threshold

compositions, one at $Z = 2.41$ as predicted by the models of Phillips and Thorpe [6, 7] and the other at $Z = 2.67$ as predicted by the model proposed by Tanaka [8]. Also there exists the chemical threshold corresponding to stoichiometry at the average coordination number $Z = 2.73$ as per the chemically ordered covalent network (COCN) model, which again lies within the glass forming region.

In the case of the Ge–Bi–Se system, the addition of a critical quantity of Bi brings about a carrier type reversal in the basic Ge–Se system [9–11]. The Ge–Se system, which is a p type semiconductor, changes into n type with the addition of 7 at.% of Bi which corresponds to an average coordination number $Z = 2.47$ for the system. The composition dependences of various physical properties such as thermoelectric power, electrical resistivity and IR absorption exhibit anomalies near this composition [12–14].

We have carried out a detailed investigation of the composition dependence of photoconductivity and carrier lifetime in the two interesting chalcogenide glass systems cited above. The temperature dependence of photoconductivity has also been analysed. The results obtained are compared with those of the parent glass compositions to obtain an insight into the effect of adding In or Bi impurities to the basic network. Experimental details, results obtained and a detailed discussion of the results are outlined in the following sections. All investigations have been on samples prepared in the bulk form.

2. Experimental method

Three sets of samples with formulae $\text{Ge}_x\text{Se}_{100-x}$ ($x = 10\text{--}40$), $\text{Ge}_x\text{In}_5\text{Se}_{95-x}$ ($x = 12\text{--}32$), and $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ ($x = 2\text{--}12$) have been prepared in the bulk form by the conventional melt quenching technique. Appropriate amounts of 5 N purity constituents are weighed in quartz ampoules and are evacuated and sealed. They are then kept in a high temperature furnace at temperatures well above their melting points for nearly 24 hours, with the ampoules rotated intermittently for uniform mixing of the constituents. The ampoules are then quenched in ice–water and are then annealed for about half an hour at temperatures well below their glass transition temperatures. The amorphous natures of the samples have been confirmed by the XRD technique and their constituents analysed by x-ray photoelectron spectroscopy (XPS).

Photoconductivities in all the samples in the bulk form have been measured by the a.c. method. The sample has been mounted in a suitable housing with a window to ensure that no light other than that from the source falls on the sample. Chopped white radiation from a 1 kW Xe arc lamp chopped at a frequency of 15 Hz has been used for excitation and the photoconductivity signal has been detected in a lock-in amplifier. This method eliminates the effect of any stray light, dark current or any other unmodulated signal or any signal modulated at any other frequency. The use of such a low frequency ensures that it is lower than the inverse of the photoconductivity response time. Carrier lifetime has been measured by the frequency resolved photo current (FRPC) technique [15, 16]. The lifetime of the carriers in the sample is related to the frequency corresponding to the peak (f_{max}) in the frequency dependence of a.c. photoconductivity through the relation $\tau = 1/2\pi f_{max}$ [15, 17].

3. Results

The temperature dependences of photoconductivity in $\text{Ge}_{20}\text{Se}_{80}$, $\text{Ge}_{20}\text{Bi}_2\text{Se}_{78}$ and $\text{Ge}_{16}\text{In}_5\text{Se}_{79}$ samples are shown in figure 1. Photoconductivity initially increases gradually with inverse temperature and then decreases in Bi as well as In doped samples. The variation shows a maximum at a particular temperature which can be identified from the slope change in the

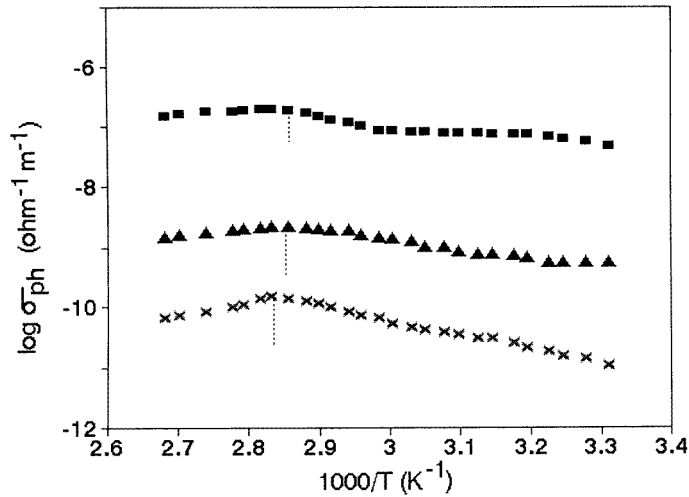


Figure 1. Variation of photoconductivity with temperature in $\text{Ge}_{20}\text{Se}_{80}$ (\times), $\text{Ge}_{20}\text{Bi}_2\text{Se}_{78}$ (\blacktriangle) and $\text{Ge}_{16}\text{In}_5\text{Se}_{79}$ (\blacksquare) glasses. Photoconductivity shows a slope change at a particular temperature which is different for different materials. Intensity of irradiated light is 25 mW cm^{-2} . Uncertainties in the measurement are within 4%.

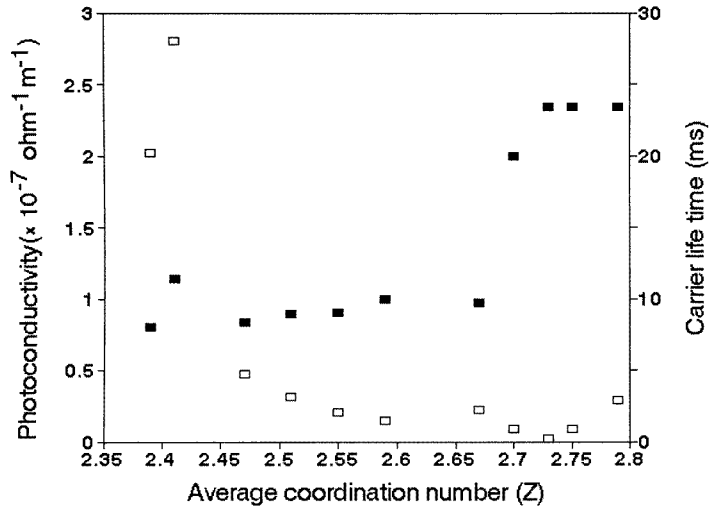


Figure 2. Variation of photoconductivity ($\square\square$) and carrier lifetime ($\blacksquare\blacksquare$) at room temperature (298 K) with average coordination number (Z) in the $\text{Ge}_x\text{In}_5\text{Se}_{95-x}$ system.

plotted curves. Figure 2 shows the composition dependence of photoconductivity and carrier lifetime in the $\text{Ge}_x\text{In}_5\text{Se}_{95-x}$ system. The average coordination number Z for each composition has been evaluated and indicated along the x -axis. A threshold maximum in photoconductivity can be observed at $Z = 2.41$ and a minimum at $Z = 2.73$. In figure 3 we plot the composition dependence of photoconductivity and carrier lifetime in the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system. As is evident from this figure, photoconductivity increases with average coordination number up to $Z = 2.46$, which corresponds to a Bi content of 6 at.%, beyond which it decreases sharply. The carrier lifetime, in general, decreases with the addition of bismuth exhibiting a sharp

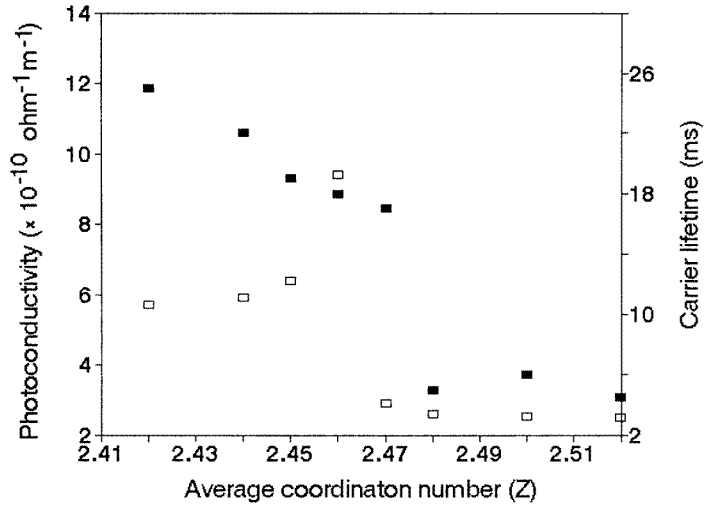


Figure 3. Variation of photoconductivity ($\square\square$) and carrier lifetime ($\blacksquare\blacksquare$) at room temperature, with average coordination number (Z) in the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system. Both photoconductivity and carrier lifetime have sharp variations around $Z = 2.46$ where the $p \rightarrow n$ transition has been found for this system.

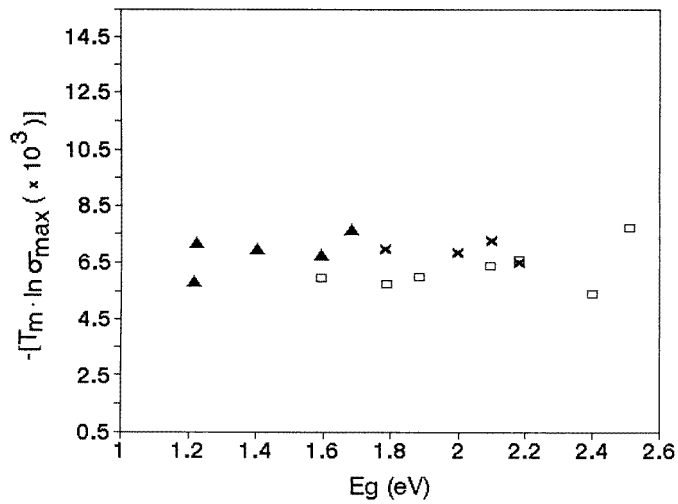


Figure 4. Variation of the optical band gap (E_g) with the product T_{max} in $\sigma_{(max)}$ for various compositions of the systems studied. Ge-Se (\times); Ge-Bi-Se (\blacktriangle); Ge-In-Se (\square). The points can be fitted to a straight line.

decrease for $Z \geq 2.47$ or $x \geq 7$ at.%. In order to analyse the nature of photoconductivity possessed by these systems we have plotted $T_m \ln \sigma_{max}$ against the optical band gap (E_g) for different compositions, where T_m is the temperature at which the photoconductivity maximum is observed and σ_{max} is the maximum value of photoconductivity. These results are shown in figure 4. These plots can be well fitted to a straight line for all the three systems investigated.

4. Discussion

Our results show that for the Ge–Se system the dark conductivity as well as photoconductivity increases by nearly two orders of magnitude with the addition of 2 at.% of bismuth and by nearly four orders of magnitude with the addition of 5 at.% of indium. The enhancement in conductivity can be interpreted as due to the enhancement in carrier density and/or mobility with doping. Increase in carrier density leads to an increase in the density of states in the gap region [18]. A number of factors determine the composition dependence of photoconductivity and carrier lifetime in these materials. These are discussed in the following paragraphs.

Selenium based chalcogenide systems are dominated by flexible twofold coordinated Se atom chains. Addition of other elements increases the cross linking between the selenium chains with the formation of different types of bond. According to the COCN model the formation of heteropolar bonds is favoured over homopolar bonds [6, 19]. The bond energies of the heteropolar bonds are, on average, higher than those of the homopolar bonds. The $\text{Ge}_x\text{Se}_{100-x}$ system can be considered as consisting of Ge–Se heteropolar bonds dispersed either in excess of Ge–Ge bonds or Se–Se bonds. Addition of indium causes a change in the nature of the structural units. In the $\text{Ge}_x\text{In}_5\text{Se}_{95-x}$ system, GeSe_2 and In_2Se_3 structural units can be considered as dispersed in Ge–Ge and Se–Se bonds. The maximum number of heteropolar bonds are formed first and the remaining valencies are satisfied by homopolar bonds. Upon analysis of different compositions, it can be seen that glass with $Z = 2.73$ consists only of structural units of GeSe_2 and In_2Se_3 with neither Se or Ge present in excess.

While analysing the composition dependence of photoconductivity and carrier lifetime, in Ge–In–Se glasses we can see a minimum in photoconductivity and a maximum in carrier lifetime at $Z = 2.73$ which corresponds to the chemical threshold of the system. These results can be explained on the basis of the COCN model outlined above. Due to the chemical ordering and higher average energy of bonds, photoconductivity assumes a minimum value at the chemical threshold. The chemical ordering causes a decrease in the number of defect states and traps in the gap region causing the carrier lifetime to attain a maximum value for this composition.

The excess conductivity due to incident radiation can be represented as [20]

$$\Delta\sigma = e(\Delta n \mu_n + \Delta p \mu_p) = eg(\tau_n \mu_n + \tau_p \mu_p) \quad (1)$$

where g is the generation rate of the carriers and τ is the carrier lifetime. Decrease in the carrier generation rate and/or mobility may be the reason for the minimum in photoconductivity at the chemical threshold composition. For the range of intensities investigated, we have plotted the variation of $\ln \tau$ with $\ln g$ for the two compositions in figure 5. From the relation $\tau = Ag^\nu$ [17], the value of the exponent ν has been evaluated. For all the samples it lies between 0.5 and 1. A value of $\nu = 0.5$ indicates bimolecular recombination and $\nu = 1$ indicates monomolecular recombination. These values of ν indicate the presence of traps in the gap state. Similar results have been obtained by Kaplan [17]. The contribution of change in mobility to change in photoconductivity could not be estimated due to the lack of sufficient experimental data.

We have determined the carrier lifetime from the relation $\tau = 1/2\pi f_{max}$, which has been interpreted as the carrier lifetime by previous workers [15, 17]. Under normal circumstances the free carrier lifetime scales with photoconductivity unless there are drastic changes in mobility. Leaving mobility apart, a reason for the observed behaviour could be the presence of multitraps in the sample. Variations in the amount of multi-trapping as the composition is varied could also play a role in determining the composition dependence of carrier lifetime. When there is multi-trapping, the carrier lifetime as determined earlier should be redefined as a photoconductivity response time.

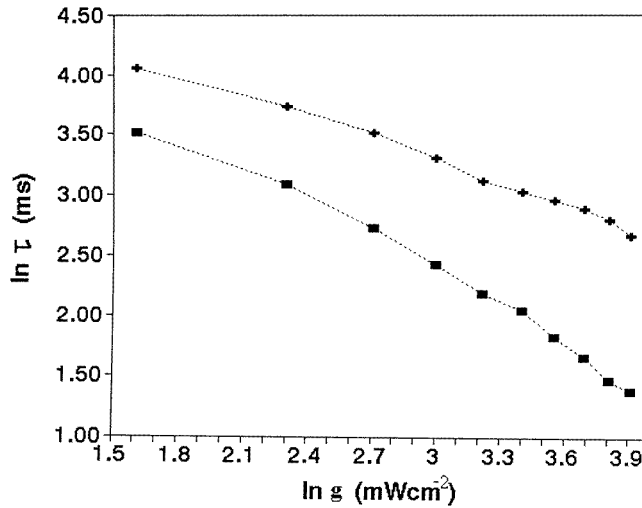


Figure 5. Variation of carrier lifetime (τ) with the generation rate of carriers (g) for the Ge–In–Se system. $\text{Ge}_{18}\text{In}_5\text{Se}_{77}$ ($Z = 2.51$), ■ and $\text{Ge}_{30}\text{In}_5\text{Se}_{65}$ ($Z = 2.75$), ++. The Ge–Bi–Se system also exhibits similar behaviour.

In addition, a sharp change in photoconductivity and carrier lifetime are observed at $Z = 2.41$. As predicted by the mechanical constraints model proposed by Phillips and Thorpe [6, 7], this composition corresponds to the one at which the system undergoes a topological transition from a floppy to rigid network. Theory predicts the occurrence of such a transition when the number of force field constraints become equal to the number of degrees of freedom. At this critical composition there is an appreciable enhancement in the density of the sample [6–8]. For this critical composition the interatomic bonds become rigid and elastic forces begin to build up fast. The network at this compositions takes the form of a fully interconnected rigid network with a number of floppy inclusions in it. The floppy inclusions result in the enhancement of photoconductivity and carrier lifetime of the material.

There are clear signatures of a p-type to n-type transition in the photoconductivity and carrier lifetime data of the Ge–Bi–Se system, shown in figure 3. In the $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system, photoconductivity rises appreciably for compositions with $x = 5$ and $x = 6$ ($Z = 2.45$ and 2.46 respectively) but decreases sharply to a low value for $x = 7$ ($Z = 2.47$) and thereafter it remains more or less constant. Carrier lifetime, in general, decreases with the addition of Bi but it shows a very sharp decrease for values of $x > 7$ at.% ($Z > 2.47$). Although the $p \rightarrow n$ transition and anomalous change of many physical properties have been analysed and explained by various authors before [9–14], the mechanism of this transition is not yet fully understood. More experimentation and modelling seem necessary to obtain 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* [10] to explain the transport mechanism in Ge–Bi–Se glasses on the basis of chemical bonds. Based on EXAFs data, Elliot and Steel [21] have attributed the mechanism to the formation of partially ionic, Bi^- chalcogen bonds and subsequent unpinning of the Fermi level.

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 around 7 at.% of bismuth. Elliot and Steel [21] have suggested that the $p \rightarrow n$ transition in these glasses is accompanied by a significant change in the local structural order

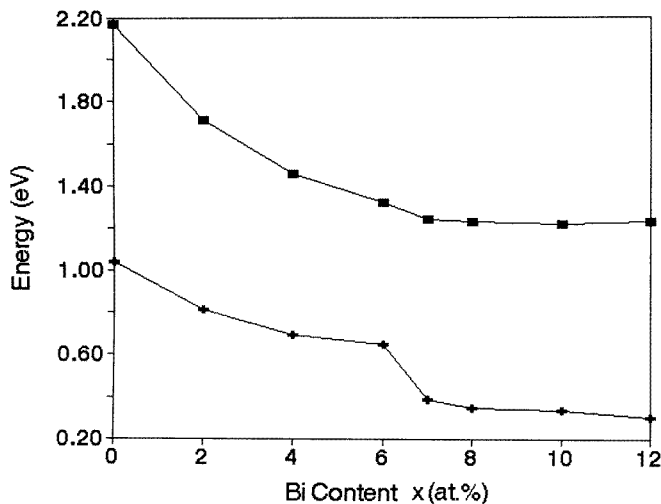


Figure 6. Composition dependent variation in optical band gap (■) and activation energy (+) of the Ge–Bi–Se system.

surrounding the Bi impurity atoms. At low Bi concentrations, the Bi–Se bonds remain covalent in character, and at high Bi concentrations they become partially ionic with slight increase in bond lengths [21]. It has also been proposed that the process of dissolution of Bi impurity in the selenium rich regions at lower concentrations produces Se^- centres making the Bi impurities positively charged. Further addition of Bi does not produce appreciable additional defects as it is entering an already modified network. Bhatia *et al* [14] have reported the variation of conductivity activation energy with composition in these samples. At low Bi concentrations there is little change in activation energy E_{av} , whereas at higher concentrations a considerable decrease in E_{av} is observed. This is explained as due to the shift in the Fermi level towards the conduction band with addition of Bi. In figure 6 we plot the variation of activation energy as well as optical band gap with Bi content. These results agree with the interpretation provided by Bhatia *et al* [14]. Other than this there is no experimental evidence in support of a change in Fermi level.

Based on the various explanations outlined above we can draw the following general conclusions regarding the observed variations in photoconductivity in Ge–Bi–Se glasses. The Ge–Bi–Se system is a pseudo-binary system with Bi atoms acting as 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 $x = 6$ at.% ($Z = 2.46$) can be interpreted as due to the formation of Bi_2Se_3 ionic bonds and the corresponding disappearance of Se–Se bonds.

While there are differences in the photoconducting properties of Ge–In–Se, Ge–Bi–Se and Ge–Se systems, they have a very important common feature. All the three systems exhibit type I photoconducting behaviour as explained by the ABFH (Arnoldussen–Bube–Fagen–Holmberg) model [22, 23]. For type I photoconductors, photoconductivity is greater than dark conductivity up to a particular temperature T_{max} , where the photoconductivity attains a maximum value. If the temperature is increased beyond T_{max} photoconductivity decreases. On the basis of the energy level diagram suggested by the ABFH model, there are transitions which are from (i) localized to extended states (for $T > T_m$) and (ii) localized to localized states (for $T < T_m$) that dominate in type I photoconductors.

In the framework of the ABFH model for type I photoconductors, the relation between maximum photoconductivity σ_{max} and optical band gap E_g can be expressed as

$$\sigma_{max} \propto \exp[-(E_{v*} + E_{\mu})/kT_{max}]. \quad (2)$$

Generally E_{v*} , the valence edge activation energy, and E_{μ} , mobility activation energy, scale with E_g . Therefore one can write [24]

$$\sigma_{max} \propto \exp[-aE_g/kT_{max}] \quad (3)$$

or

$$T_{max} \ln \sigma_{max} \propto -aE_g. \quad (4)$$

In the case of the three systems under investigation, the plot between E_g and the product $T_m \ln \sigma_{max}$ is found to be nearly a straight line which is in tune with their type I behaviour.

The photoconductivity activation energy is generally very small, being only 10–15% of the optical band gap. In the present samples it varies from 0.1 to 0.2 eV. Consequently the slope of the $\log \sigma_{ph}-1/T$ variation (figure 1) is very small below T_m but is definitely finite. This also confirms the type I nature of photoconductivity in these materials [24].

5. Conclusions

Our results indicate that the photoconducting properties of chalcogenide glasses can be improved by the addition of metallic impurities such as Bi or In. Significant variations in photoconductivity and carrier lifetime have been observed in the Ge–In–Se system at compositions corresponding to the chemical and mechanical thresholds. The photoconductivity and carrier lifetime in the Ge–Bi–Se system are found to exhibit sharp changes near the composition exhibiting p \rightarrow n transition. The observations are explained based on the COCN model for amorphous semiconductors. Variation of photoconductivity with temperature is analysed based on the ABFH model and the systems investigated are found to be type I photoconductors. The addition of impurities do not change this character for the systems studied.

Acknowledgments

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