

## EFFECT OF BISMUTH ON THE ELECTRICAL PROPERTIES OF a-Ge<sub>20</sub>Se<sub>80</sub> GLASSES

G. Singh, J. Sharma, A. Thakur, N. Goyal, G. S. S. Saini, S. K. Tripathi\*

Centre of Advanced Study in Physics, Panjab University, Chandiharh-160 014, India

The present paper reports the effect of Bi impurity (low ~ 4 at. % and high ~ 10 at. %) on the ac conductivity ( $\sigma_{ac}$ ) of a-Ge<sub>20</sub>Se<sub>80</sub> glass. Frequency dependent ac conductance and capacitance of the samples over a frequency range of 100 Hz to 50 kHz has been taken in the temperature range of 268 K to 360 K. At frequency 2 kHz and temperature 298 K, the value of ac conductivity ( $\sigma_{ac}$ ) decreases at low concentration of Bi (4 at. %). However, the value of  $\sigma_{ac}$  increases at higher concentration of Bi (10 at. %). The ac conductivity is proportional to  $\omega^s$  for undoped and doped samples. The value of frequency exponent (s) decreases as the temperature increases. The dielectric constant (k) slightly decreases at low Bi concentration and increases at higher Bi concentration. These results have been explained on the basis of some structural changes at low and higher concentration of Bi impurity.

(Received July 4, 2005; accepted July 21, 2005)

*Keywords:* Chalcogenides, Hopping conduction, Defect states

### 1. Introduction

Germanium Selenium system exhibits properties, which are unusual, and possibly unique, relative to other semiconductors. These unusual characters have obviously added much flavour to the stimulated study. Amorphous semiconductors from Se-based system such as Ge<sub>x</sub>Se<sub>1-x</sub> have attracted much attention in recent years. Ge<sub>x</sub>Se<sub>100-x</sub> is being actively investigated as high efficiency semiconductors for xerography, switching and memory devices and reversible phase change optical recording [1-3]. Exposure to light or heat that excites electron-hole pairs produces structural changes in nearly all chalcogenide glasses. The results change with atomic configuration and a subsequent change in the physical properties such as structure, optical and electrical properties of the material [4, 5].

The physical properties of these glasses are influenced by the presence of inherent defects. The doping (p or n type) of these glasses had been a serious problem in the past as most of these glasses showed p type conduction even after incorporation of various impurities. However, it has been reported [6, 7] that Ge<sub>20</sub>Se<sub>80-x</sub>Bi<sub>x</sub> alloys show a sign reversal of thermo power from p to n type at a fairly large concentration of Bi ( $x \geq 7$  at. %). Two mechanisms have been proposed to understand the n-type conduction in these Bi-doped glasses. The first one is based on the evidences for the phase separation at microscopic level due to the presence of Bi<sub>6</sub><sup>-</sup> atoms [8, 9]. The second one is based on the structural studies due to the presence of positively charged Bi<sub>3</sub><sup>+</sup> or Bi<sub>4</sub><sup>+</sup> atoms [10,11]. In the first case, the n-type conduction is due to the microcrystallites of n-type conducting c-Bi<sub>2</sub>Se<sub>3</sub> embedded in the rest of glassy matrix while on the contrary, in the second case, it is due to the relative decrease in inherent D<sup>+</sup> defects. However, studies on the role played by defects in bringing out n-type conduction in Bi doped glasses are very rare. These inherent defects in chalcogenide glasses originate in the rearrangements taking place at the prevalent chain ends (D<sup>+</sup> and D<sup>-</sup> charged dangling bonds or C<sub>3</sub><sup>+</sup> and C<sub>1</sub><sup>-</sup> intimate valence-alternation pair, IVAP) [12,13]. These defects give rise to the states in the gap and affect the transport mechanism in chalcogenide glasses.

---

\*Corresponding author: surya@pu.ac.in; surya\_tr@yahoo.com

The present paper reports the temperature and frequency dependent ac conductivity of  $(\text{Ge}_{20}\text{Se}_{80})_{100-x}\text{Bi}_x$ , where  $x = 0, 4$  and  $10$  at. %. Measurements indicate that how the electrical properties of  $\text{Ge}_{20}\text{Se}_{80}$  change after the doping with Bi. These interesting results have been explained on the basis of the structural changes occurring in the material due to the doping of Bi. Section 2 describes the experimental details. The results have been presented and discussed in section 3. The last section deals with the conclusion of this work.

## 2. Experimental

For the present work, the glassy materials have been prepared by taking the constituent elements (99.999% pure) in required atomic weight percentages. The materials were then mixed together and the mixture was sealed in a quartz ampoule (length  $\sim 10$ cm, diameter  $\sim 1$ cm) under a pressure of  $\sim 10^{-5}$  Torr. These ampoules were mounted in a furnace for heating. In the beginning, the temperature of the furnace was raised slowly and kept constant at melting temperature of constituent elements (271 K for Bi, 490 K for Se, and 1210 K for Ge) for about two hours each. The temperature was then raised and maintained at about 50 K more than the highest melting point of the constituents (1260 K) for about 24 hours. The ampoules were immediately cooled in liquid nitrogen, for the material to go into the glassy state. The glassy materials, in the form of ingots, were obtained by breaking the ampoules. To verify the amorphous nature of glasses, the X-ray diffraction (XRD) study on all samples was done (Philips X-ray generator, model PW1729 along with a PW1710 diffractometer). No peaks have been observed for the materials prepared by above-mentioned technique, thereby confirming that the prepared materials are amorphous in nature.

Compressed pellets are prepared by grinding the bulk-ingots into fine powder and compressing the powder in a die under a hydraulic press (pressure  $10^6$  Kg/m<sup>2</sup>). While making compressed pellets, one must ensure that the powder is compressed to maximum compaction so that there are no voids in the sample. A three terminal sample holder has been fabricated for the measurement of ac conductivity of the pellet shaped samples. Provision has been made for measuring the vacuum inside the sample holder. Besides that, a thermocouple has been inserted inside the sample holder and is kept close to the sample for the measurement of correct temperature. A built in micrometer has been provided for the measurement of sample thickness. Cylindrical brass jacket has been used as outer cover to provide excellent electromagnetic shielding. A low temperature bath (Julabo F-70 VC/K) has been used for controlling the temperature of the samples. Vacuum pumping system (model VS-65D, H.H.V India) has been used to achieve a vacuum, up to  $10^{-4}$  to  $10^{-5}$  Torr inside the sample holder. A general Radio Bridge (Model 1615-A) was used for the measurements of frequency dependent ac conductivity and dielectric constant of the materials having large resistivity. The bridge consists of an audio oscillator (model 1311), a tuned amplifier (model 1232-A) and a null detector, which permits balance to a resolution of one part in a million. This bridge is designed for the precise measurements of capacitance and conductance. Its direct read-out system minimizes the reading errors and permits rapid operation.

## 3. Results and discussion

Figs. 1-3 show the frequency dependence of measured conductivity for the undoped  $\text{Ge}_{20}\text{Se}_{80}$  and doped  $(\text{Ge}_{20}\text{Se}_{80})_{96}\text{Bi}_4$  and  $(\text{Ge}_{20}\text{Se}_{80})_{90}\text{Bi}_{10}$  samples respectively at different temperatures. From these figures, it is clear that  $\sigma_{ac} = A\omega^s$ , where  $s$  is frequency exponent and  $A$  is a constant. The decrease in slope with increasing temperature indicates that the value of  $s$  decreases with increasing temperature.

Fig. 4 shows the temperature dependence of the frequency exponent  $s$  for all the samples. It is clear from the figure that the value of  $s$  decreases with the increasing temperature and with the increase in doping concentration. This decrease is more in case of higher Bi (10 at. %) doping concentration as compared to the lower Bi (4 at. %) concentration. At low temperatures, this value of  $s$  approaches the same in case of low Bi concentration with the undoped one.

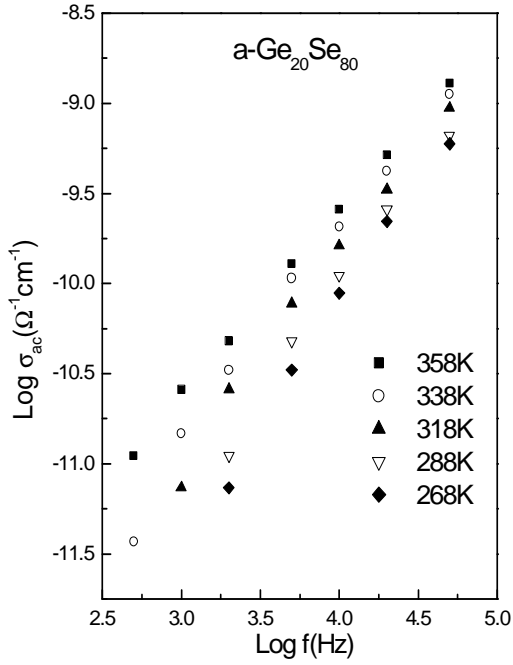


Fig. 1. Frequency dependence of conductivity at different temperatures.

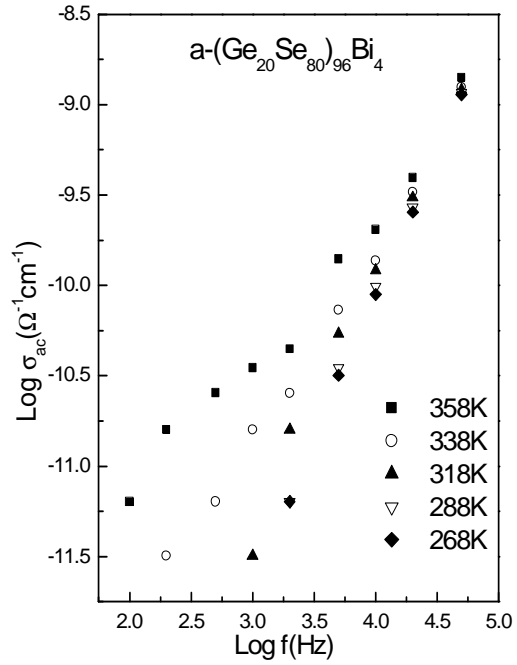


Fig. 2. Frequency dependence of conductivity at different temperatures.

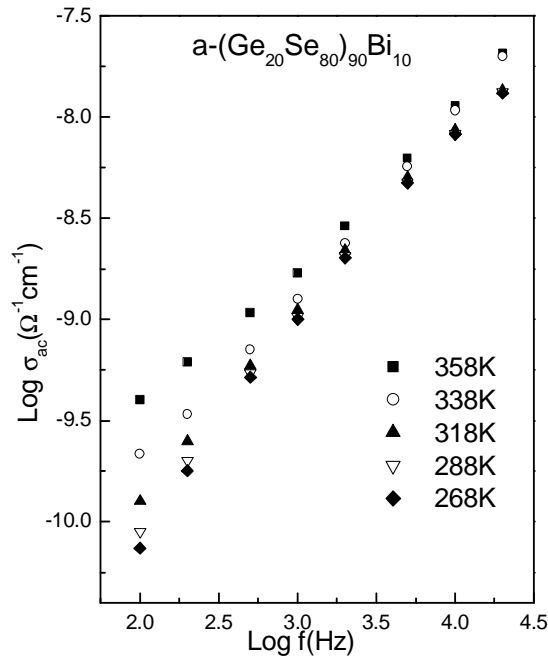


Fig. 3. Frequency dependence of conductivity at different temperatures.

The decrease in  $s$  is more at higher temperatures in both Bi concentrations. However, at high concentration of Bi (10 at. %), this value of  $s$  is always less as compared to the undoped one at all temperatures. Figs 5-8 show the frequency dependence of  $k$  at the four different temperatures for  $\text{Ge}_{20}\text{Se}_{80}$ ,  $(\text{Ge}_{20}\text{Se}_{80})_{96}\text{Bi}_4$  and  $(\text{Ge}_{20}\text{Se}_{80})_{90}\text{Bi}_{10}$  samples.

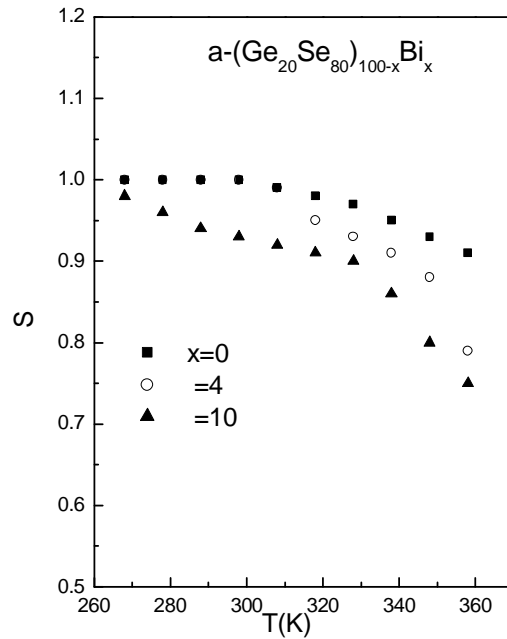


Fig. 4. Variation of frequency exponent  $s$  with temperature.

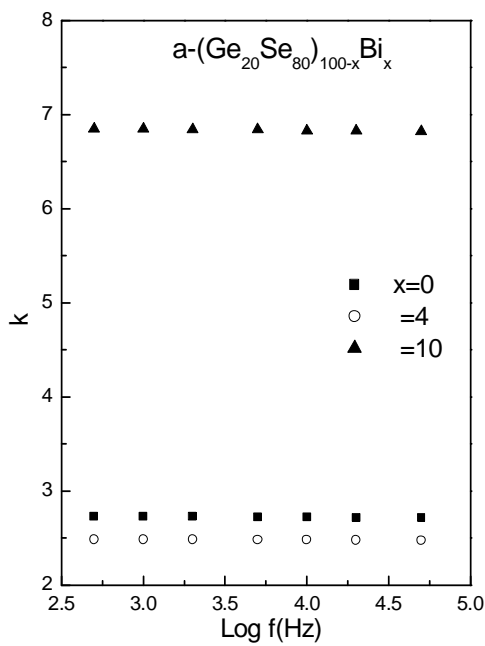


Fig. 5. Variation of dielectric constant  $k$  with frequency at 268 K.

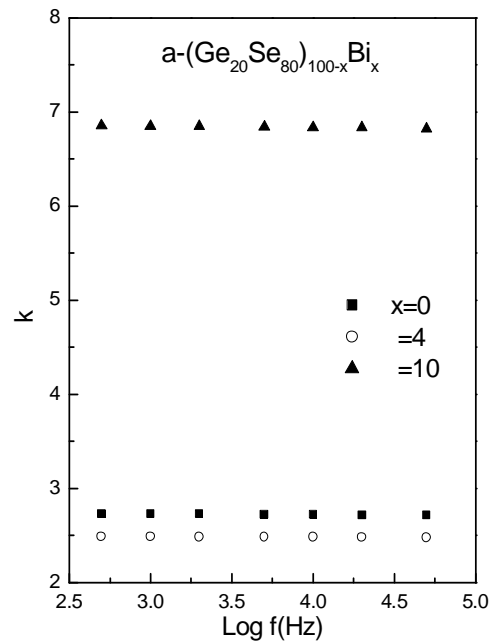


Fig. 6. Variation of dielectric constant  $k$  with frequency at 288 K.

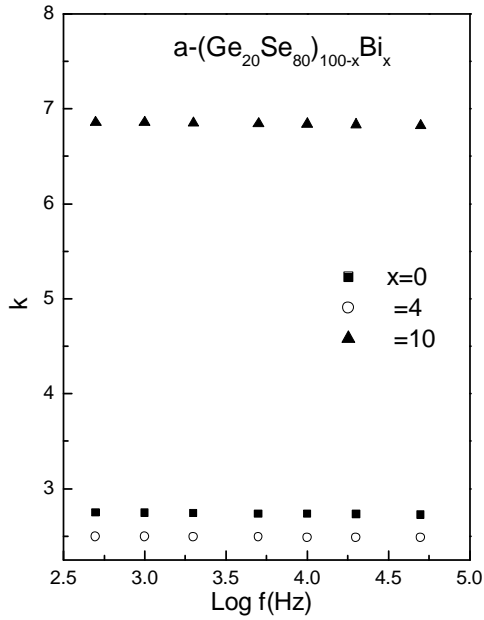


Fig. 7. Variation of dielectric constant k with frequency at 318 K.

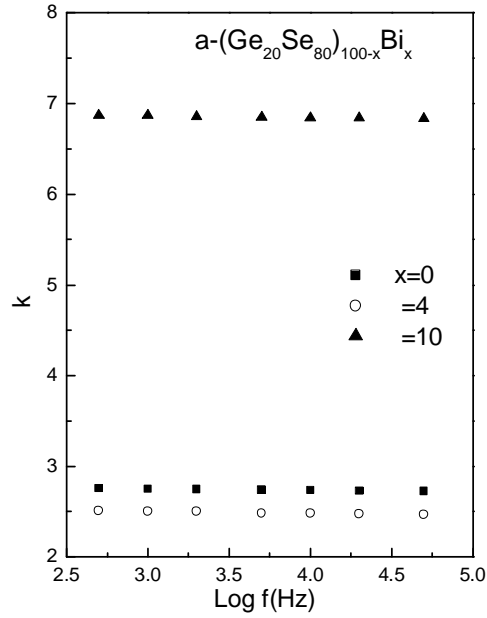


Fig. 8. Variation of dielectric constant k with frequency at 388 K.

These figures indicate that the value of k decreases in case of low concentration of Bi as compared to the doped sample. However, a reversal in the trend occurs at higher concentration of Bi. The value of k increases in case of high Bi concentration (10 at. %).

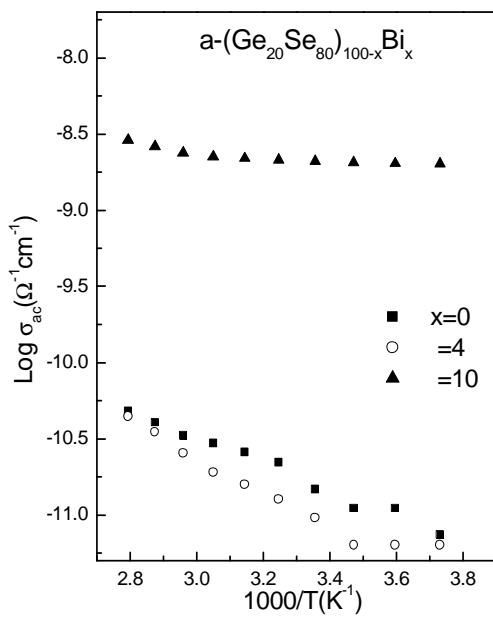


Fig. 9. Temperature dependence of ac conductivity at 2 kHz.

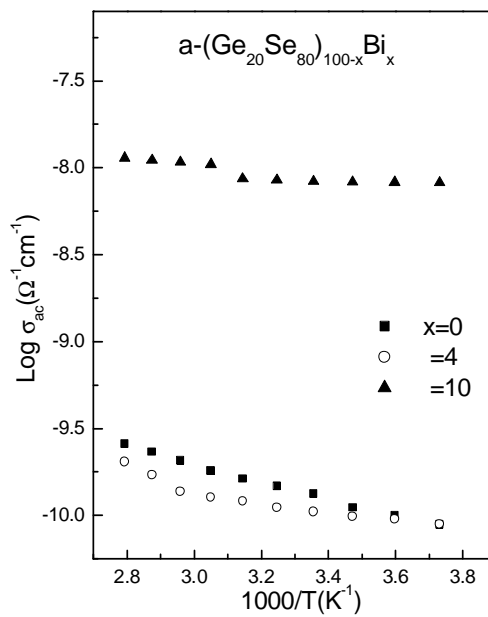


Fig. 10. Temperature dependence of ac conductivity at 10 kHz.

Figs. 9-11 show the temperature dependence of ac conductivity of  $\text{Ge}_{20}\text{Se}_{80}$ ,  $(\text{Ge}_{20}\text{Se}_{80})_{96}\text{Bi}_4$  and  $(\text{Ge}_{20}\text{Se}_{80})_{90}\text{Bi}_{10}$  samples at 2 kHz, 10 kHz and 20 kHz respectively. From the figures, it is clear that the value of conductivity increases with temperature more in case of pure and low doped samples. However, in case of higher doping concentration of Bi, the increase in conductivity is small with temperature. The conductivity of  $\text{Ge}_{20}\text{Se}_{80}$  slightly decreases in case of low Bi concentration, particularly at higher temperatures. However, a large increase in conductivity has been observed at higher Bi concentration at all temperatures. Figs. 12 and 13 show the temperature dependence of  $k$  at two different frequencies 2 kHz and 20 kHz. These figures indicate that the value of  $k$  is slightly less than the undoped sample in case of Bi (4 at. %) concentration at all temperatures. However, this value increases drastically in case of high Bi concentration (10 at. %) at all temperatures.

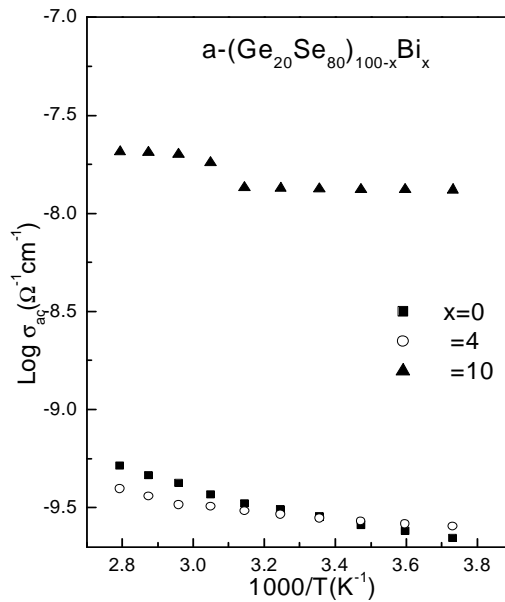


Fig. 11. Temperature dependence of ac conductivity at 20 kHz.

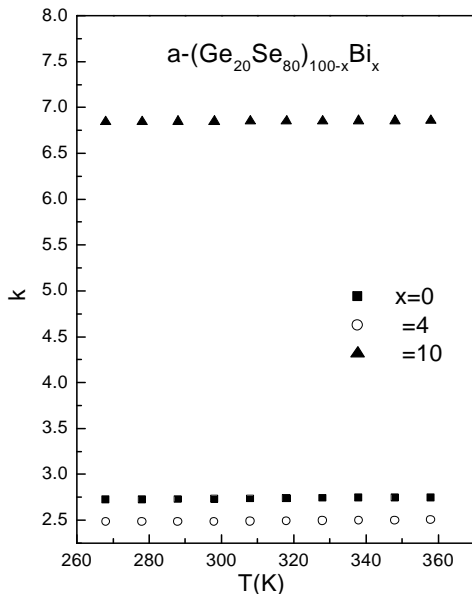


Fig. 12. Variation of dielectric constant with temperature at 2 kHz.

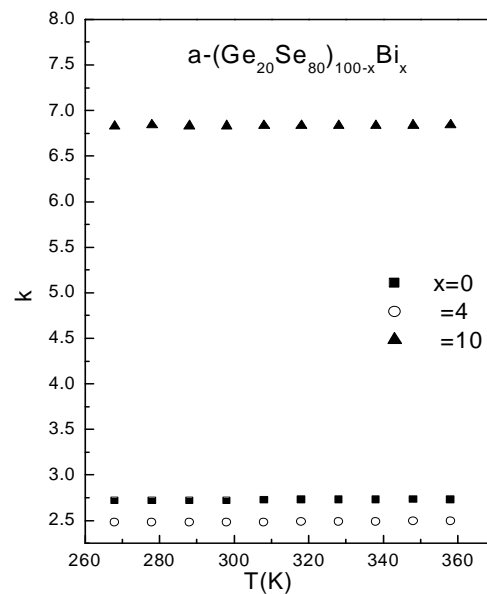


Fig. 13. Variation of dielectric constant with temperature at 20 kHz.

Using a modified Correlated Barrier Hopping Model (CBH) [14,15], the above results can be easily explained. According to this model:

$$\sigma_{ac} = \frac{n}{24} \pi^2 NN_p \varepsilon' \omega R_\omega^6 \quad (1)$$

where  $n$  is the number of polarons involved in the hopping process,  $R_\omega$  is the hopping distance for the condition  $\omega\tau=1$  and is given by [14]:

$$R_\omega = \frac{4ne^2}{\varepsilon' \{ \omega + kT \ln(\omega\tau) \}} \quad (2)$$

The value of frequency exponent  $s$  is calculated from equations (2) and (3), and is equal to:

$$S = \frac{d(\ln \sigma_{ac})}{d(\ln \omega)} = 1 - \frac{6kT}{W - kT \ln[1/\omega\tau_0]} \quad (3)$$

$NN_p$  is given by:

$$NN_p = N_T^2 \quad (\text{For bipolaron hopping}) \quad (4)$$

where  $N_T$  is the number of density of states.

$$NN_p = N_T^2 \exp(-U_{eff}/2kT) \quad (\text{For single polaron hopping}) \quad (5)$$

The total conductivity is the combined mechanism of these processes. These processes are bipolaron hopping between  $D^+$  and  $D^-$  centers, single polaron hopping between  $D^0$  and  $D^-$  centers and  $D^0$  and  $D^+$  centers. Here,  $W$  is equal to  $W_M$ , which is slightly less than the band gap for bipolaron hopping. However, it is equal to  $W_1$  and  $W_2$  for the two types of single polaron hopping, which are substantially less than  $W_M$  for bipolaron hopping. The smaller values of  $W_1$  and  $W_2$  for single polaron hopping means that the value of  $R_w$  is much greater for single polaron hopping as compared to bipolaron hopping Eq. (2).

Earlier, experimental studies have shown that addition of Bi in  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  brings down the optical gap from 2.0 eV at  $x = 0$  to nearly 1.2 eV for n-type conducting samples [7]. Tohge *et al.* [16] have also observed an increase in the photoconductivity drastically after the Bi addition. Bhat *et al.* [17] have shown the role of defects in carrier type reversal in Bi doped Ge-Se glasses by photoluminescence spectroscopy. They have shown the compositions at lower Bi content exhibit luminescence with fine features associated, while the compositions that show n-type conduction do not exhibit luminescence. The identification of the associated fine features, carried out by deconvoluting the experimental spectra, reveals that Bi addition brings out a relative diminishing in  $D^+$  defects as compared to  $D^-$  ones. This is possible, if Bi atoms added enter the glassy matrix as positive defects. For Bi to go as positive defect, it has to have a coordination number of less than its valence i.e. 5. Earlier structural studies like EXAFS, Raman and IR showed that the coordination number of Bi is three with positive charge on it. Takahashi [18] has shown a reduction in hole drift mobility as compared to electron drift mobility with the addition of Bi. This can be understood as the  $D^+$  and  $D^-$  defects act as electron and hole traps respectively.

So, Bi having coordination number three appears more convincing as it can be made consistent even with the phase separation evidences [9]. This Bi atom, which exists as positively charged defects with three nearest Se neighbours in Ge-Se glassy matrix, brings out an imbalance in  $D^+ - D^-$  defect pairs. An additional consequence of Bi atoms entering as  $\text{Bi}_3^+$  defects in the glassy matrix is the availability of extra electrons in the conduction band extended states [19]. These two changes combined with the setting in of microscopic inhomogeneties in the form of a- $\text{Bi}_2\text{Se}_3$  can lead to a condition where in the Fermi level ( $E_F$ ) can no longer be pinned [9]. A shift in  $E_F$  towards the conduction band brings out n-type conduction at higher Bi content in  $\text{Ge}_{20}\text{Se}_{80}$  glass.

So, it is clear from the above discussions that the addition of Bi changes the carrier type reversal (p-n transition) in  $\text{Ge}_{20}\text{Se}_{80}$  glass. As the doping concentration increases, the bipolaron hopping contribution decreases due to the decrease in the density of defect states. But single polaron hopping contribution is going to increase because of the shift of the Fermi level towards the conduction as discussed earlier. Due to the shift of  $E_F$  towards conduction band,  $W_2$  will decrease and it seems that single polaron hopping starts to dominate over bipolaron hopping at higher Bi doping concentration (i.e. 10 at. %).

#### 4. Conclusions

Electrical conductivity measurements have been done in undoped  $\text{Ge}_{20}\text{Se}_{80}$  and doped with Bi low and high concentrations. Frequency dependent ac conductivity measurement at different temperatures show that the value of conductivity slightly decreases at low concentration (4 at. %) of Bi and increases drastically at higher concentration of Bi (10 at. %). Dielectric constant also follows the same pattern at low and high Bi concentrations. The value of  $\epsilon$  decreases at both concentrations at high temperature. It is observed that the addition of Bi brings out a reduction in the relative concentration of  $\text{D}^+$  as compared to  $\text{D}^-$  defects. This imbalance accompanied by the contribution of extra electrons brings out n-type conduction in Bi doped glasses. Due to the shift of the Fermi level, single polaron hopping starts dominating over bipolaron hopping at higher concentration of Bi.

#### Acknowledgements

This work is financially supported by the C.S.I.R. (major project), New Delhi. GS and AT are grateful to UGC and CSIR, New Delhi respectively for providing financial assistance.

#### References

- [1] N. Thoge, Y. Yamamoto, T. Minami, M. Tanaka, *Appl. Phys. Lett.* **34**, 640 (1979).
- [2] Z. L. Mao, H. Chen, Iien Jung-AI, *J. Appl. Phys.* **78**, 2338 (1995).
- [3] R. M. Mehra, A. Ganjoo, G. Kaur, P. C. Mathur, *J. Thermal Anal.* **45**, 405 (1995).
- [4] A. V. Kolobov, H. H. Yoneyagi, K. Tanaka, K. Tanaka, *J. Non-Cryst. Solids* **198**, 709 (1996).
- [5] Kojihayashi, D. Kato, K. Shimakawa, *J. Non-Cryst. Solids* **198**, 696 (1996).
- [6] R. Mathur, A. Kumar, *Sol. Stat. Commun.* **59**, 163 (1986).
- [7] N. Tohge, T. Minami, Y. Yamamoto, M. Tanaka, *J. Appl. Phys.* **51**, 1048 (1980).
- [8] J. C. Philips, *Phys. Rev. B* **36**, 4265 (1987).
- [9] N. A. Bhat, K. S. Sangunni, *Sol. Stat. Commun.* **116**, 297 (2000).
- [10] T. Ikari, T. Tanaka, K. Ura, K. Maeda, K. Futagami, S. Shigetomi, *Phys. Rev. B* **47**, 4984 (1993).
- [11] G. Saffarini, J. M. Saiter, A. Zamilan, *J. Optoelectron. Adv. Mater.* **3**, 485 (2001).
- [12] R. A. Street, N. F. Mott, *Phys. Rev. Lett.* **35**, 1293 (1975).
- [13] M. Kastner, D. Adler, H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
- [14] K. Shimakawa, *Phil. Mag. B* **46**, 123 (1982).
- [15] K. Shiakawa, *Phil. Mag. B* **48**, 778 (1983).
- [16] N. Tohge, T. Takahiro, Y. Yonesakim, T. Minami, *J. Appl. Phys.* **58**, 4225 (1985).
- [17] N. A. Bhat, K. S. Sangunni, K. S. R. K. Rao, *J. Optoelectron. Adv. Mater.* **3**, 735 (2001).
- [18] T. Takahashi, *J. Non-Cryst. Solids* **44**, 239 (1981).
- [19] O. Matsuda, T. Ohba, M. Taniguchi, *J. Non-Cryst. Solids* **198**, 688 (1996).