

Temperature and Composition Dependence of Electrical Conductivity of $\text{Ge}_{10}\text{Se}_{90-x}\text{Bi}_x$ ($x=0, 2, 4, 6, 8, 10$) Chalcogenide Glasses

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ABSTRACT

Electrical conductivity of $\text{Ge}_{10}\text{Se}_{90-x}\text{Bi}_x$ ($x=0, 2, 4, 6, 8, 10$) glassy systems prepared by melt quenching technique has been studied at different temperature in bulk form through I-V characteristic curves. It has been observed that the electrical conductivity increases as the Bi concentration increases up to 4 atomic weight percentages and on further addition of Bi it reduces. The variation in electrical conductivity with Bi concentration is attributed to the Se-Bi bond concentration. Using the Arrhenius equation of conductivity, the activation energy of conduction is evaluated. The effect of Bi concentration on activation energy has also been studied. It is quite evident from results that Poole-Frankel and Recharadson-Schottky conduction mechanism hold good for conduction in these glasses.

Keywords: Amorphous semiconductor, Quenching technology, Chalcogenide glasses

1. INTRODUCTION

Electrical conductivity is a powerful technique for the study of ion transport process [01]. The effects of impurities on the electronic properties of chalcogenides have been controversial since their discovery. Earlier it was believed that they are insensitive to the various added impurities as each impurity atom could satisfy its valance requirement by adjusting its nearest neighbor environment. However it has been shown that the effect of charged additives in a lone pair semiconductor depends on whether the charged additives equilibrate or not with valance alternation defects. Recent experiments revealed that the addition of impurity atoms (like Bi) to chalcogenide glasses produces a remarkable

change i.e. p to n-type conduction. It has been shown that Ni ions with keV energy implanted in thin film of a-As₂Se₃ can induce doping effects. The electrical properties of the amorphous semiconducting thin films can thus be modified. For more than two decades ion beam techniques have successfully been used to address central issues in the physics of amorphous semiconductor materials. The results of these investigations are becoming useful for diverse areas of application ranging from the fabrication of large area opto-electronic devices to the production of *sub μm* optical patterns for lithography and data storage.

Models of defects proposed by many author have successfully explained many physical features in chalcogenide glasses [02]. These models predict that

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the relative concentration of defects can be controlled by chemical additives of some metallic impurities, when introduced, at high sufficient temperatures, into the glass to attain its stoichiometric state. The use of thin film polycrystalline semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. The technological interest in polycrystalline based devices is mainly caused by their very low production costs. Thin films now occupy a prominent place in basic research and solid state technology. Many of the technology in recent years have been mainly due to the ability to prepare not only structurally and chemically pure crystals but also crystals with a controlled impurity. The role that thin films have played in some of these advances is well established [03-04]. Semiconductors play an important role in the fabrication of active thin film devices [05]. The IV-VI compounds lead sulphide (PbS), lead selenide (PbSe) and lead telluride (PbTe), often referred to collectively as lead salts, are extremely interesting semiconductors. They have been the subject of considerable research due to the technological importance of these materials, in crystalline and polycrystalline forms, as detectors of infrared radiation and more recently as infrared emitters and solar control coating also [06-07]. Indeed, the lead salts exhibit properties which are unusual and possibly unique, relative to other semiconductors, and these unusual characteristics have obviously added to the stimulated study. A particularly unusual feature of this group of materials is the relative stability of the lattice over a rather wide range of non-stoichiometry. The temperature coefficient (dE_g/dT) of the minimum energy gap E_g is positive for these compounds while it is negative for all other compound semiconductors. The semiconductors PbS, PbSe and Pbte show a small direct gap at the L point of the hydrostatic pressure [08-09] and increases with temperature [10-11]. Further the static dielectric constants of the lead salts are unusually large when

compared with values for other semiconductors. The rock salt structure lead chalcogenide narrow gap semiconductors and their alloys have been applied in long wavelength imaging [12], diode lasers [13], and in thermo photovoltaic considerable interest because of their use in infrared lasers and photovoltaic and photoconductive detectors [14, 15]. In particular, commercial lead salts detectors in the form of sensitized polycrystalline films have been widely used. They have also found increasing application in the fabrication of diode lasers, which are powerful tools in IR gas spectroscopy [16-17]. This is because these alloys possess the important characteristics that their band gap varies with composition and can also be fine tuned by other means, e.g., by varying the temperature, pressure etc. [18]. The development of laser technology has opened up new applications for IV-VI compounds. The laser diodes based on lead chalcogenides and their alloys are important sources for the tunable radiations in the mid infrared wavelength region. They are considered to be mainly utilized for detecting hydrocarbon pollutants in atmosphere, high resolution spectroscopy, trace gas analysis and optical fiber communication system over super long distances [19-20]. The optical, electrical and structural properties of PbS are studied in the present article. The transport properties of the material are of great importance in determining whether the material is congruent with our necessities or not. Conductivity is an important factor, which reveals important and reliable information about the transport phenomenon and other physical properties of the materials.

2. EXPERIMENTAL

Glassy alloy of $Ge_{10}Se_{90-x}Bi_x$ ($x=0, 2, 4, 6, 8, 10$) were prepared by quenching technique. The exact proportion of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-

120) with the least count of 10-4gm. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules length ~ 6 cm and were internal diameter ~ 8 mm). The sealed ampoules containing were heated to 950°C and were held at that temperature for 10 hours inside a furnace. The temperature of the furnace was raised slowly at a rate of $3-4^\circ\text{C}/\text{minute}$. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod on which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys. After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by x-ray diffraction patterns. Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The coplanar structure (length ~ 1.2 cm and electrode separation ~ 0.5 mm) was used for present measurements. The electrical conductivities in dark as well as in presence of light were studied by counting them in a specially designed sample holder in which illumination could be achieved through a transparent window. A vacuum of about 10^{-4} Torr was maintained throughout these measurements. The temperature of the film was controlled by mounting the heater inside the sample holder and measured by a calibrated chromel alumel constantan thermocouple mounted very near to the films. The heating rate was kept quite small (0.5 K/min.) for these measurements. For I-V measurements in bulk, pellets of 13 mm diameter and thickness ~ 1 mm were prepared under a load of 5 tons. These pellets were used in circuitry of Keithley electrometer 6517A in order to record the I-V Characteristics.

3. CHARACTERIZATION

Chemical composition of the thin film was determined by XRF. An XRF plot For $\text{Ge}_{10}\text{Se}_{90-x}\text{Bi}_x$ where ($x=0,2,4,6,8,10$) alloy thin is shown in Fig. 1. The amorphous city of thin film was confirmed by the absence of any sharp peaks in the X-ray diffraction patterns.

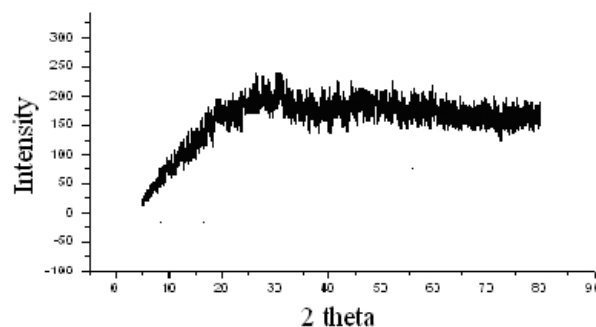


Fig. 1: XRD pattern of $\text{Ge}_{10}\text{Se}_{90-x}\text{Bi}_x$ (Where $x=0,2,4,6,8,10$) chalcogenides glasses at room temperature

I-V characteristics of $\text{Ge}_{10}\text{Se}_{90-x}\text{Bi}_x$ ($x=0,2,4,6,8,10$) glassy pellets were carried out in a temperature range from room temperature to 355 K. Fig.2 shows the temperature dependence of I-V characteristic of $\text{Ge}_{10}\text{Se}_6\text{Bi}_4$ as a representative case.

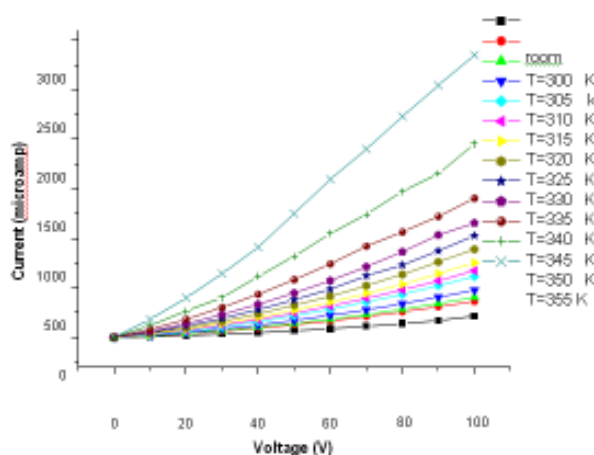


Fig. 2: I-V characteristics of $\text{Ge}_{10}\text{Se}_6\text{Bi}_4$ glassy pellets at different temperature

4. RESULT AND DISCUSSION

To explain the behavior of the observed I-V characteristics in these glasses, different mechanisms have been considered here and a discussion is initiated. It can be noticed that the I-V curves show ohmic behavior in the region A-B. Above the point B the curve start to deviate from linearity and the relation between the current and the square root of the applied voltage is given by Jonscher and Hill [22]

$$I = I_{\text{PF}} \exp (\hat{a} V^{1/2} / kT) \quad (1)$$

where $\hat{a} = (e^3 / 4 \delta \hat{a}_0 d)^{1/2}$, $\hat{a}_0$ is the permittivity of the space, $\hat{a}$ is the relative permittivity of the sample, d is the inter-spacing between the filled and empty sites (jump distance) and I_{PF} (at $V=0$) is given by

$$I_{\text{PF}} = I_0 \exp (-\tilde{O} / kT) \quad (2)$$

Where $\tilde{O}$ is the trap depth and $I_0 = (A n e \tilde{\nu})$, since A , n , e and $\tilde{\nu}$ are the electrode area, carrier concentration, electronic charge and phonon frequency, respectively. The constant $\tilde{\nu}$ is taken as 10^{13} s^{-1} [23].

Fig. 3 shows the plot between $\ln(I)$ vs $V^{1/2}$ for $\text{Se}_{90}\text{In}_{10-x}\text{Sb}_x$ glassy pellet. Linearity of $\ln(I)$ vs $V^{1/2}$ curves suggests that the conduction in such material obey the Poole-Frankel conduction mechanism. The observed linearity could be due to absence of space charge resulting in uniformity of field distribution between electrodes. The current in case of Poole-Frankel effect will practically remain unchanged when polarities of the electrodes are reversed. This is due to the fact that current does not depend upon the potential barrier at the interface. The Poole-Frankel conduction mechanism deals with the conduction in such materials where defect/ impurity generated electron, traps are involved. The structural defects in the material cause additional energy states close to the band edge called 'traps'. These traps restrict the current flow because of the capture and emission process, thereby becoming the dominant current mechanism.

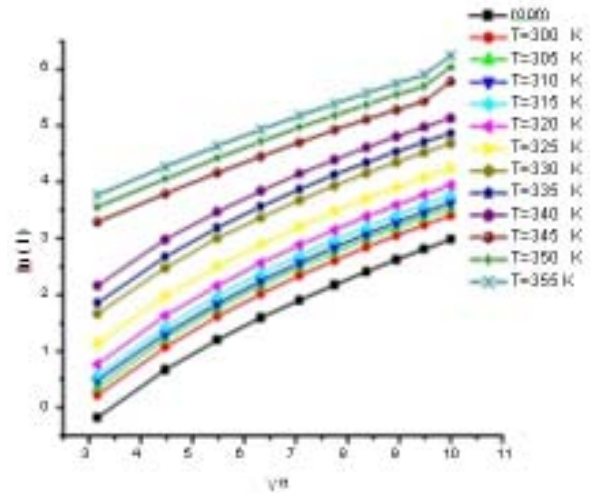


Fig 3 (a) $\text{Ge}_{10}\text{Se}_{90}$

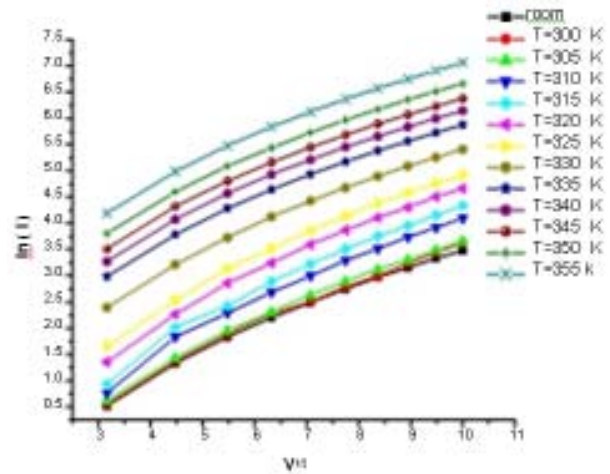


Fig 3 (b) $\text{Ge}_{10}\text{Se}_{88}\text{Bi}_2$

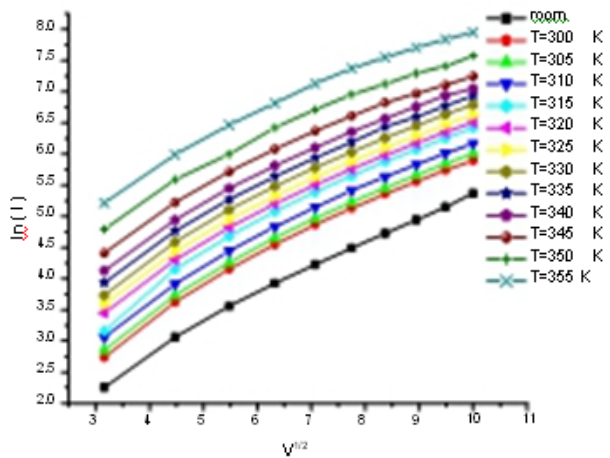


Fig.3 (c) $\text{Ge}_{10}\text{Se}_{86}\text{Bi}_4$

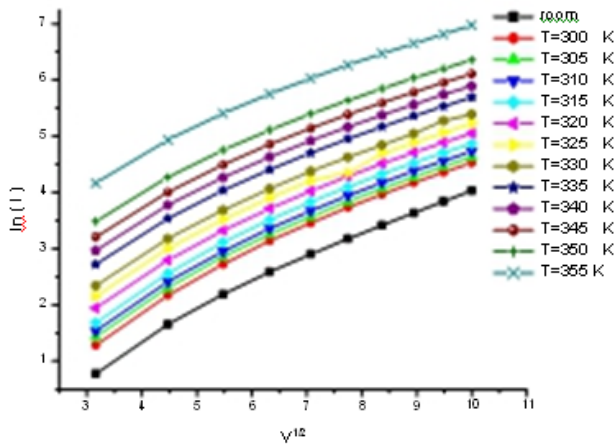


Fig.3 (d) $Ge_{10}Se_{84}Bi_6$

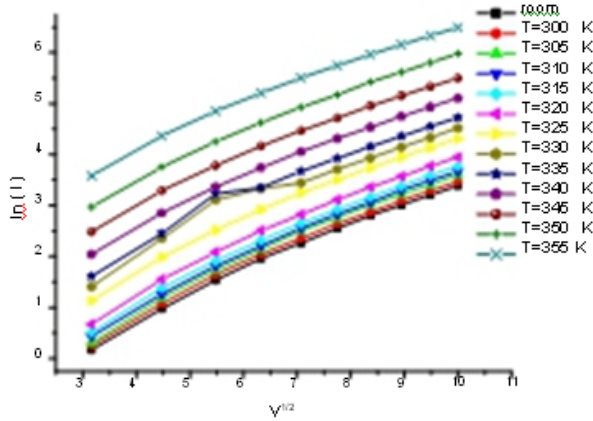


Fig.3 (e) $Ge_{10}Se_{80}Bi_8$

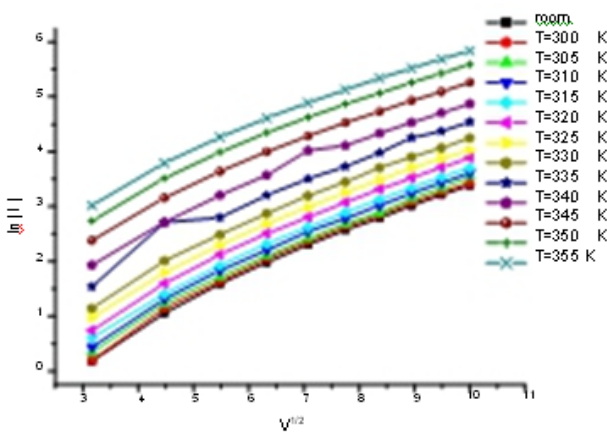


Fig.3 (f) $Ge_{10}Se_{80}Bi_{10}$

Fig. 3: $\ln(I)$ versus $V^{1/2}$ of the system $Ge_{10}Se_{90-x}Bi_x$ ($x=0, 2, 4, 6, 8, 10$) at different temperature

Current voltage relation of Recharadson-Schottky is given as:

$$J=AT^2 \exp(-\frac{e}{kT} + \hat{a} E^{1/2}) \quad (3)$$

$$\text{With } \hat{a} = \left(\frac{e}{kT} \right) \left(\frac{e}{4\pi\epsilon_0 d} \right)^{1/2} \quad (4)$$

Where the symbol have their usual meanings. Fig.4 shows the plot of $\ln(J)$ against temperature for $Ge_{10}Se_{86}Bi_4$ glassy system and we get two linear region in this plot. The non-linearity or sharp increase in current between the temperature ranges 335 K to 355 K indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature, which may be regarded as glass transition temperature and it is also supported by DSC thermo gram of the samples reported earlier [24]. As the temperature increases beyond 335 K i.e. glass transition range, nucleation and growth process starts and the glassy system leads to crystallization. With the growth of the grain, the size of grain increase with the narrowing down to grain boundaries which in turn affect the conduction process. This is due to the fact that available charge carriers will get the easier path to cross the grain boundaries, which is effectively responsible for the increment in the current in the temperature range beyond 335 K. Also this decrease in the resistance in this temperature range is caused due to the fact that glass is acquiring a more ordered state during the process of crystallization.

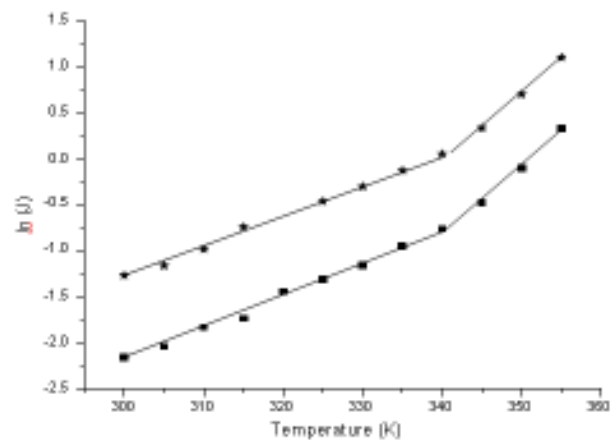


Fig. 4: The plot of $\ln(J)$ against temperature for $Ge_{10}Se_6Bi_4$ glassy system at two different voltages

DC electrical conductivity was calculated from the relation:

$$\sigma_{\text{DC}} = 1/\tilde{n}_{\text{DC}} = (1/R)(L/A) \quad (5)$$

Where, R is the resistance of the sample, L is the thickness of the sample, A is the cross-sectional area of the sample and $\tilde{n}_{\text{DC}}$ is the resistivity of the sample under test. It is well known that electrical conduction can take place by means of two parallel processes namely band conduction and hopping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states at high temperatures. The excitations of carriers into localized states at band edges cause the hopping conduction. Thus the total conductivity is given as:

$$\sigma = \sigma_i + \sigma_h \quad (6)$$

where, σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

Fig. 5 shows the composition vs. conductivity plots at different temperatures. It has been indicated that in Se containing glass, there is a tendency to form polymerized network glasses and the homopolar bond is qualitatively suppressed [25]. Moreover, at lower percentage of Bi the system contains $\text{BiSe}_{4/2}$ tetrahedral units dissolved in a matrix composed of Se chains. With the increases of Bi content, the glassy matrix becomes heavily cross-linked and the static hindrance increases. The Se-Se bonds (bond energy 205.8 KJ/mol) will be replaced by Bi-Se bonds, which have a higher bond energy (214.2 KJ/mol). Hence the cohesive energy of the system increases with increasing Bicontent. It is found that electrical conductivity is maximum at 4 at % of bismuth (Bi). This composition can be considered as a critical composition at which the system becomes a chemically ordered alloy containing high-energy Bi-Se heteropolar bonds. Further addition of Bi favours the formation of Bi-Bi bonds (bond energy 176.4 KJ/mol) thus reducing the Bi-Se bond concentration. Thus the cohesive energy decreases resulting a decrease of conductivity.

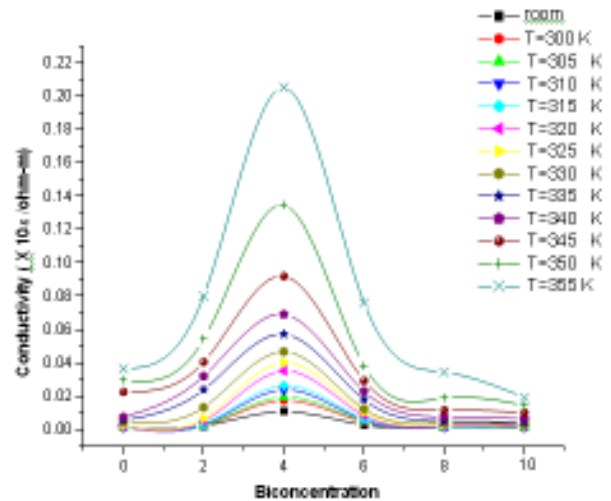


Fig. 5: Conductivity vs. Biconcentration at different temperature

The variation of electrical conductivity with temperature of different glassy alloys is shown in Fig. 6. It is found that at low temperature electrical conductivity increases linearly. The non-linearity or sharp increase in current between the temperature ranges 335 K to 355 K indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature as explained above.

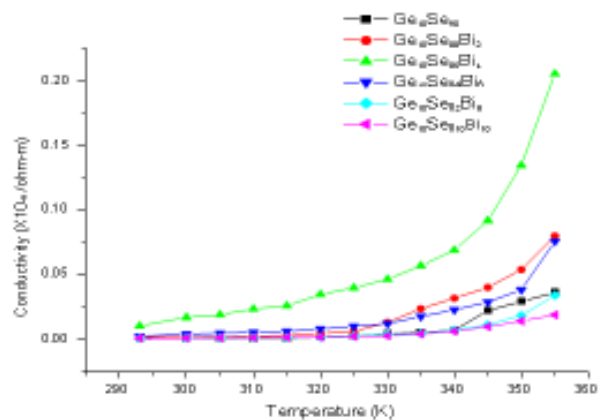


Fig. 6: The variation of electrical conductivity with temperature of different glassy alloys

The Dc conductivity of the investigated samples is plotted against $(1/T)$ and is found to satisfy the Arrhenius relation

$$\sigma = \sigma_0 \exp (-E_c / RT) \quad (7)$$

Where E_c is the activation energy of conduction and σ_0 is the pre-exponential factor. Fig.7 Shows the variation in $\ln(\sigma)$ as a function of $10^3/T$, for various Ge-Se-Bi glassy alloys. Fig.7 Shows break lines; their kinks illustrate two different values of activation energy for each sample. These may reveal two different conduction mechanisms, depending on the temperature range. The activation energies at low and high temperature ranges, for each sample, have been deduced and given in Table 1.

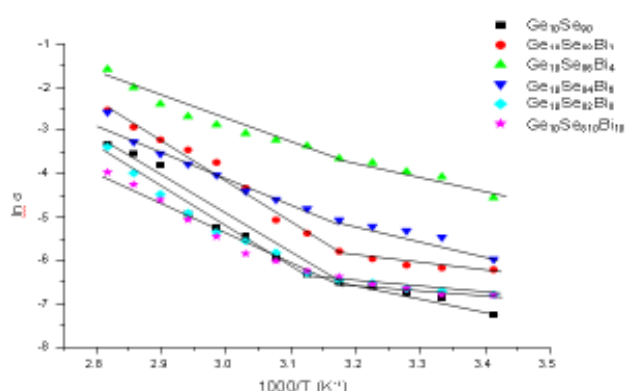


Fig.7: Shows the variation in $\ln(\sigma)$ as a function of $10^3/T$, for various Ge-Se-Bi glassy alloys

Table 1: The activation energies at the low and high temperature ranges.

Sample	335-355 K		Room temp -335 K	
	E_c (KJ/mol)	σ_0 ($\times 10^3$ /ohm-m)	E_c (KJ/mol)	σ_0 ($\times 10^3$ /ohm-m)
Ge ₁₀ Se ₉₀	80.25	3.16	25.21	1.17
Ge ₁₀ Se ₈₈ Bi ₂	77.66	3.14	22.25	1.04
Ge ₁₀ Se ₈₆ Bi ₄	44.06	2.48	30.91	2.01
Ge ₁₀ Se ₈₄ Bi ₆	53.36	2.62	30.17	1.84
Ge ₁₀ Se ₈₂ Bi ₈	69.52	2.62	11.45	0.74
Ge ₁₀ Se ₈₀ Bi ₁₀	74.92	3.03	21.94	0.72

It can be seen that the activation energy in the low temperature range is almost composition independent for all the samples. This may mean that, in low temperature range, the sensitivity of the investigated samples for conduction is somewhat weak at high concentration of Bi. The activation energy in the high temperature range decreases as the Bi concentration increase up to 4 atomic weight percentages and more addition of Bi reduces the activation energy. As the

bismuth content increases beyond 4, more Bi-Bi and Se-Bi bonds may be formed, this increases the cross-link density in the structure. This is turning increases the compactness of the structure, which consequently results in an increase of the activation energy for conduction. Fig.8 shows variation of activation energy with Bi concentration in 335-355-temperature range.

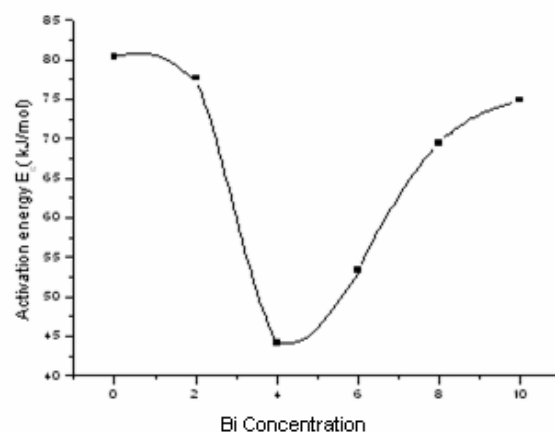


Fig.8: Variation of activation energy with Biconcentration in 335-355-temperature range.

5. CONCLUSION

The I-V characteristics of Ge₁₀Se_{90-x}Bi_x have been discussed and explained in terms of their parent structure related to Se-Bi system in the addition of Bi inclusion. Also the conduction is explained qualitatively in terms of Poole Frankel and Recharadson-Schottky conduction mechanism. More precisely we conclude that:

- The electrical conductivity increases up to 4 at. wt % of Bi and decreases on further addition of Bi.
- The electrical conductivity increases with the increase in temperature, which confirms the semi conducting nature of the samples.
- The activation energy of conduction of these glassy alloys has been calculated using Arrhenius equation in Two different temperature ranges. In low temperature range activation energy is almost independent of Bi concentration but in high

temperature range the activation energy decreases up to 4 at. Wt. % of Bi and increases on further addition of Bi.

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