

Electrical transport properties of amorphous $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ films

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D.C. Conductivity measurements on the thin films of a $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ system (where $x = 0, 0.5, 2$ and 4) are reported in the temperature range $213\text{--}390$ K and the density of states (DOS) near the Fermi level is calculated using dc conductivity data. It is found that the conduction in all the samples takes place in the tails of localized states. The conduction in the high temperature region $296\text{--}390$ K is due to thermally assisted tunneling of electrons in the localized states at the conduction band edge. In the low temperature region $213\text{--}296$ K conduction takes place through variable range hopping in the localized states near the Fermi level. © 2003 Kluwer Academic Publishers

1. Introduction

Chalcogenide glasses have attracted much attention because of their potential application in solid state devices. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. Moreover they are interesting as core materials for optical fibers for transmission especially when short length and flexibility are required [1]. The current interest in chalcogenide materials centers on x-ray imaging [2] and photonics. Recently one could observe a keen interest in bismuth-tellurium alloys, due to the fact that they possess promising thermoelectric properties at low temperature [3]. Simultaneously such materials may be applied for optical recording of information [4], laser diode [5] etc. A large number of proposals were devoted to the creation of different kinds of corresponding superlattices of bismuth-telluride-type layers [6–8].

The effect of an impurity in amorphous semiconductors may be widely different depending upon the conduction mechanism and the structure of the material [9]. While in crystalline semiconductors the effect of a suitable impurity is always to provide a new donor or acceptor state, this is not essential in amorphous semiconductors [10]. The variation of conductivity with temperature in the two cases can be quite similar. For example, in the case of amorphous materials, the conductivity in the high temperature region is either due to thermally activated tunneling of the carriers in the localized states near the mobility edges or is due to band conduction of the carriers in the extended states [11]. In the low temperature region the hopping conduction in amorphous materials is either of an activated type or is due to variable range hopping in the localized states near the Fermi level [9]. Investigation of the temperature dependence of conductivity, the effect of isoelectronic and non-isoelectronic impurities on the activation energy and the effect of a high electric field on the conduction

mechanism is a subject of great interest because the results of such studies provide ways to control effectively the conductivity of amorphous semiconductors. Recently various workers [12–14] have reported the use of these materials for reversible optical recording by amorphous to crystalline phase change. Se-Te has been used as a base material and the incorporation of Bi as a third element has been studied. The introduction of third element expands the glass forming area, and also creates compositional and configurational disorder in the system. Generally, the binary alloys are covalent in nature and the addition of third element creates ionic-covalent bonds and as result the conduction increases. We have chosen Bi because of its special role on the type of conduction [15]. The chalcogenide materials usually show p-type conduction. Tohge *et al.* [16] and Negals *et al.* [17] reported that the type of conduction changes from p to n-type when $\text{Bi} \geq 7$ at.%. This change is related to the chemistry of the system and consequently a change in the Fermi level [18]. Several workers have added different elements to Se-Bi system [19–23], and most of these materials exhibit a p-type to n-type transition [24–26].

In the present study, the d.c. Conductivity of thin film amorphous samples of a $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ system has been studied in order to find the effect of Bi alloying. Various Mott's parameters α , T_0 , R , $N(E_F)$, W , αR etc. have been calculated for these samples exhibiting variable range hopping conduction in the low temperature region.

2. Experimental

Glassy alloys of a $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ ($x = 0, 0.5, 2$ and 4) were prepared by melt-quenching technique. Materials of 99.999% purity were sealed in quartz ampoules (length ~ 12 cm, internal diameter ~ 0.8 cm) with a vacuum of about 10^{-3} Pa. The sealed ampoules were

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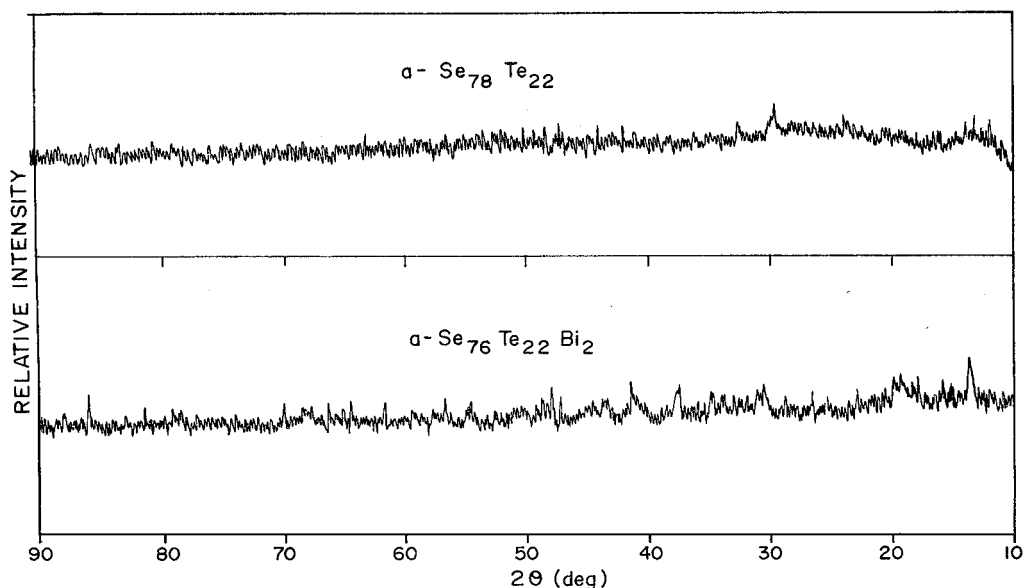


Figure 1 (a) X-ray diffraction pattern of a-Se₇₈Te₂₂, (b) X-ray diffraction pattern of a-Se₇₆Te₂₂Bi₂.

kept inside a furnace where the temperature was raised slowly (3–4°C min⁻¹) to 900°C. The ampoules were rocked frequently for 10 hours at the maximum temperature to make the melt homogeneous. Quenching was done in ice water.

X-ray diffraction traces of all the four samples were taken at room temperature and found to show almost similar trends. Therefore, only two of them (for a-Se₇₈Te₂₂ and a-Se₇₆Te₂₂Bi₂ samples) are shown in Fig. 1. The absence of sharp structural peaks in these x-ray diffraction traces confirmed the amorphous nature of the samples. Thin films of these glassy alloys were prepared by vacuum evaporation technique using a standard coating unit. Well-degassed corning glass plates having predeposited indium electrodes were used as a substrate for depositing films in the planer geometry (length ~1.2 cm) and different electrode gap. These films were prepared by evaporation technique using molybdenum boats and keeping the substrate at room temperature at a base pressure of 10⁻³ Pa. The thickness of the films was of the order of 5000 Å. The films were kept in the deposition chamber in dark for 24 h before mounting them in the sample holder. This was done to attain a metastable thermodynamic equilibrium in the samples as suggested by Abkowitz [27]. The deposition parameters were kept almost the same for all samples so that a comparison of results could be made.

For the measurement of Mott parameters, the samples were mounted in a specially designed metallic sample holder where a vacuum of about 10⁻¹ Pa could be maintained throughout the measurement. A d.c. Voltage (1.5 V) was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 617). The temperature was measured by mounting a calibrated copper-constantan thermocouple near the sample.

3. Results and discussion

The variation of d.c. conductivity with temperature ($\ln \sigma$ vs T^{-1}) for a-Se_{78-x}Te₂₂Bi_x (0 ≤ x ≤ 4) is shown in Fig. 2. In all the samples, the plots of $\ln \sigma_{dc}$ versus

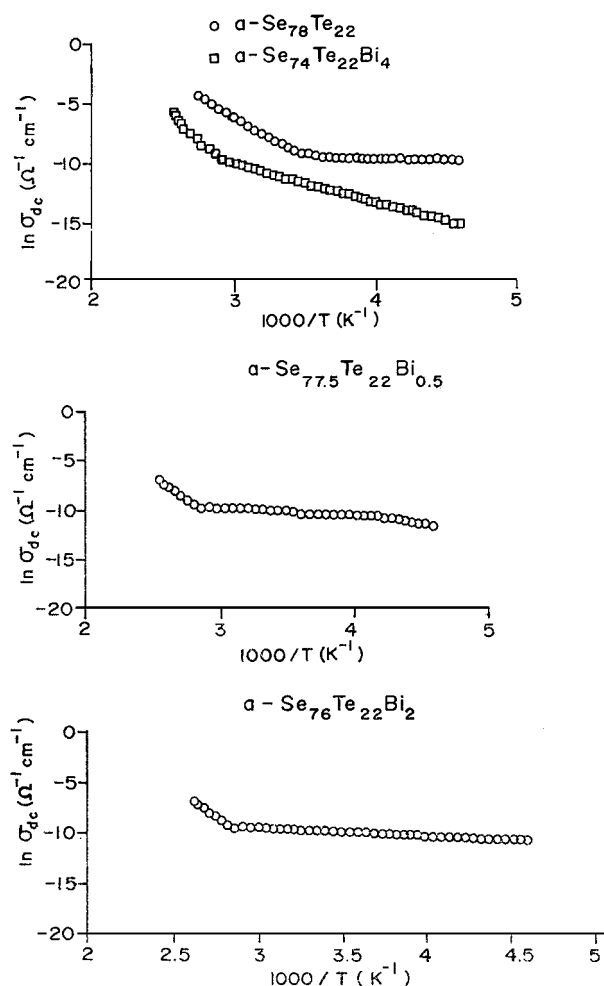


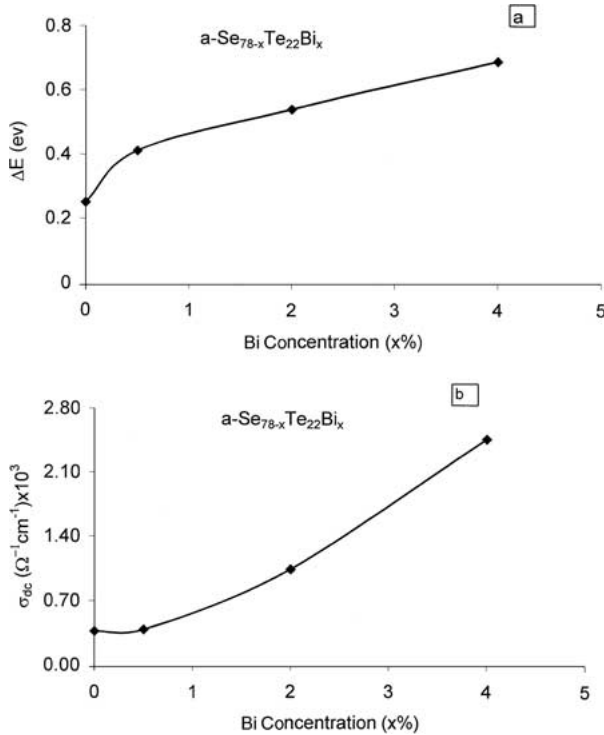
Figure 2 Temperature dependence of dc conductivity in the temperature range (213–390 K) at various concentration of Bi in a-Se_{78-x}Te₂₂Bi_x system.

$1000/T$ are straight lines, indicating that the conduction in these glasses is through an activated process in the temperature range (296–390 K). The dc conductivity can, therefore, be expressed by the usual relation

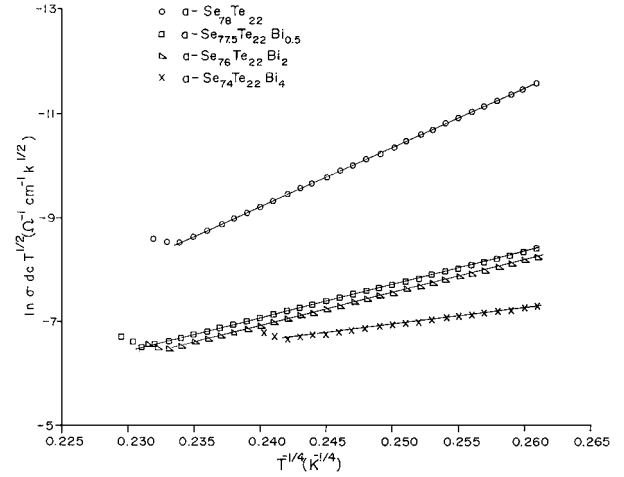
$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

TABLE I Electrical parameters of a-Se_{78-x}Te₂₂Bi_x system at $T = 373$ K

Sample	$\sigma_{dc}(\Omega^{-1} \text{ cm}^{-1})$	$\Delta E(\text{eV})$	$\sigma_0(\Omega^{-1} \text{ cm}^{-1})$	$X_c(\text{Electronegativity})$
a-Se ₇₈ Te ₂₂	3.69×10^{-4}	0.55	9.22×10^3	2.10
a-Se _{77.5} Te ₂₂ Bi _{0.5}	3.87×10^{-4}	0.71	1.27×10^6	2.09
a-Se ₇₆ Te ₂₂ Bi ₂	1.04×10^{-3}	0.78	3.98×10^7	2.08
a-Se ₇₄ Te ₂₂ Bi ₄	2.47×10^{-3}	0.86	1.10×10^9	2.07


 Figure 3 (a) Dc conductivity (σ_{dc}) vs Bi concentration (X%) in a-Se_{78-x}Te₂₂Bi_x at 373 K. (b) Activation energy (ΔE) vs Bi concentration (X%) in a-Se_{78-x}Te₂₂Bi_x system.

where σ_0 is pre-exponential factor, ΔE is activation energy and k is Boltzmann constant. The values of ΔE and σ_0 are given in Table I for these films suggest the conduction to be due to thermally assisted tunneling of charges in the localized states present in the band tails. The values of σ_{dc} and ΔE increase with increase of Bi content in Se-Te system as shown in Fig. 3. The calculated values of the thermal activation energies further show the Fermi level to be fixed well away from the band edges in the forbidden gap. It may, however, be mentioned that the activation energy ΔE alone does not provide any indication as to whether conduction takes place in the extended states above the mobility edge or by hopping in the localized states. This is because of the fact that both these conduction mechanisms can occur simultaneously, with the conduction via localized states dominating at low temperatures. The activation energy in the former case represent the energy difference between mobility edge and Fermi level, $E_c - E_F$ or $E_F - E_V$, while in the later case it represents the sum of the energy separation between the occupied localized states and the Fermi level $E - E_F$, and the mobility activation energy for the hopping process between the localized states. In order to obtain a clear distinction between these two conduction mechanism, Mott [28] has suggested that the pre-exponential factors σ_0 of Equation 1


 Figure 4 $\ln \sigma_{dc} T^{1/2}$ vs $T^{-1/4}$ plot at various concentration of Bi in a-Se_{78-x}Te₂₂Bi_x system.

for conduction in the localized states should be two to three orders smaller than for conduction in the extended states, and should become still smaller for conduction in the localized states near the Fermi level. For conduction in the extended states the values of σ_0 reported for a-Se and other Se alloyed films are of the order of $10^4 \Omega^{-1} \text{ cm}^{-1}$ [11], while in the present case the values of σ_0 varying from 9.22×10^3 to $1.10 \times 10^9 \Omega^{-1} \text{ cm}^{-1}$. The increase in the value of σ_0 with the increase of Bi content shows that the mobility of charge carriers in the trap states increases with increasing Bi concentration. The increase in σ_{dc} and ΔE is due to the decrease in the density of localized states in the mobility gap.

At a low temperature, both the conduction mechanisms occur simultaneously, i.e. conduction in extended states and conduction via localized states. Fig. 2 shows the two conduction regions at a particular temperature, below which the plot deviates from linearity. Therefore, the low temperature data for these samples have been reported as $\ln \sigma_{dc} (T)^{1/2}$ vs $T^{-1/4}$ as shown in Fig. 4. The conductivity in the temperature region 213–269 K increases slowly with increasing in temperature which suggests that the conduction is due to variable range hopping in the localized states near the Fermi level. It may be mentioned here that when sufficient phonon energy is available, the hopping is thermally assisted and is in between nearest neighbors in accordance with Equation 1. On the other hand, when the phonon energy is insufficient, the more energetic phonon-assisted hops becomes favourable, as a result of which the carriers will tend to hop larger distance in order to locate sites which are energetically closer than that of nearest neighbors. This variable range hopping conduction mechanism is characterized by Mott's [28–31] expression of the form:

$$\sigma(T) = \sigma'_0 / \sqrt{T} \exp(-AT^{-1/4}) \quad (2)$$

where

$$A^4 = T_0 = \lambda \alpha^3 / kN(E_F) \quad (3)$$

$N(E_F)$ is the density of localized states at the Fermi level, α^{-1} is the degree of localization, T_0 is the degree of disorder, λ is a dimensionless constants and k is the Boltzmann constant. The value of pre-exponential term σ'_0 of Equation 2 as obtained by various workers [9, 30, 31] is given by

$$\sigma'_0 = 3e^2 \gamma [N(E_F) / 8\pi \alpha k T]^{1/2} \quad (4)$$

Where e is electron charge and γ is Debye frequency ($\sim 10^{13}$ Hz). Simultaneous solution of Equations 3 and 4 yields

$$\alpha = 22.52 \sigma'_0 A^2 \text{ cm}^{-1} \quad (5)$$

and

$$N(E_F) = 2.12 \times 10^9 \sigma_0'^3 A^2 \text{ cm}^{-3} \text{ eV}^{-1} \quad (6)$$

The hopping distance is given by [31]

$$R = [9/8\pi \alpha k T N(E_F)]^{1/4} \quad (7)$$

The hopping energy is also given by [31]

$$W = 3/4\pi R^3 N(E_F) \quad (8)$$

It may be mentioned that it is difficult to distinguish Equations 1 and 2 on the basis of conductivity temperature variation. The only possible distinction that can be made is on the basis of the value of αR and W , which according to Mott [31] should have a value greater than unity and KT respectively for variable range hopping conduction. Various Mott parameters A , σ'_0 , $N(E_F)$, T_0 , α , W , and αR , etc. have been calculated from Equations 2–8 and are given in Table II. It is found that the value of W , α and T_0 decreases on increasing Bi concentration. Since T_0 represent the degree of disorder and α^{-1} the degree of localization, it follows that the amorphicity of the samples decreases on increasing Bi concentration. It is also evident from Table II that the density of localized states $N(E_F)$ decreases from 10^{27} to 10^{16} $\text{eV}^{-1} \text{ cm}^{-3}$ respectively and is plotted in Fig. 5. The use of Mott's formula, however, yields unreasonably high values for the density of localized states $N(E_F)$; for example, 3.56×10^{27} $\text{eV}^{-1} \text{ cm}^{-3}$ for a- $\text{Se}_{78}\text{Te}_{22}$ sample. This discrepancy in the Mott Parameters has therefore been removed by recalculating the Mott parameters [32] using a constant value of α . For our systems, we have chosen the value of α to be 10^7 cm^{-1} . Greaves *et al.* [33] reported the value of $N(E_F)$ as 3×10^{17} $\text{eV}^{-1} \text{ cm}^{-3}$ for amorphous arsenic films by assuming α^{-1} to be 9 \AA . The calculated values

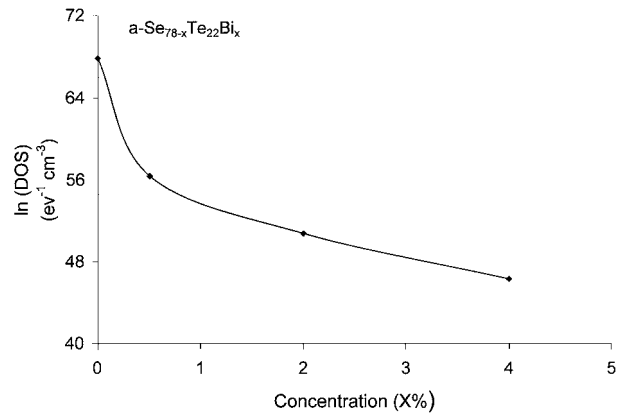


Figure 5 Concentration (X) vs density of states $N(E_F)$ curves in a- $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ by dc conductivity.

of various Mott's parameters are given in Table III. It is evident from the table that the density of localized states $N(E_F)$ increases from 10^{21} to 10^{22} with increasing Bi concentration. These results are similar to those obtained by other workers [34, 35] on chalcogenide glasses. It is also evident from Tables II and III that the values of αR and hopping energy W remain almost the same, irrespective of the value of α , which may be evaluated with the help of Mott's prefactor σ'_0 or can be assumed to be a constant. This variation can be explained in terms of charged impurity in the structure of Se-Bi. Schotmiller *et al.* [36] have studied the effect of the addition of various elements (sulphur, tellurium, arsenic and germanium) on the structure of glassy selenium using infrared and Raman spectroscopy. They reported that in glassy selenium, about 40% of the atoms have a ring structure and 60% of the atoms are bonded as polymeric chains. Tellurium based glasses contains short chains, while Se based glasses contain a mixture of long chains and Se_8 rings. An introduction of Te decreases the Se ring concentration with an increase in long Se-Te polymeric chains and mixed rings [37], which makes the system more rigid. However, at higher concentrations of Te, the possibility of Te-Te bonding may also exist. Parthasarathy and Gopal [38] have also assumed the creation of new defect states only after a particular concentration of Te (>8 at.% in their case) to explain their pressure dependent conductivity results. According to them, below a certain concentration of Te, the structure of Se does not change significantly and hence the bond pictures remain unaltered. On the addition of Bi, Bi-Se bonding is developed which reduces the number of defects in the system. The Bi-Se bond concentration increases with Bi concentration while the bond between chalcogen atoms such as Se-Te decreases [39]. We have calculated the hopping energy (W) at low temperatures and the values obtained are consistent with results obtained by other workers [40] for amorphous films. Another possible distinction that

TABLE II Mott parameters for a- $\text{Se}_{78-x}\text{Te}_{22}\text{Bi}_x$ temperature region (213–296 K)

X(Bi%)	$A(\text{K}^{1/4})$	T_0 (K)	σ'_0 ($\Omega^{-1} \text{ cm}^{-1}$)	α (cm^{-1})	R cm (243 K)	$N(E_F)$ ($\text{eV}^{-1} \text{ cm}^{-3}$)	W (meV) (243 K)	αR
0.0	86.66	5.64×10^7	25.43×10^4	1.03×10^{10}	8.27×10^{-10}	3.56×10^{27}	118.6	8.48
0.5	53.33	8.09×10^6	6.90×10^3	1.74×10^7	3.00×10^{-7}	1.21×10^{20}	72.9	5.22
2.0	46.66	4.74×10^6	1.16×10^3	3.17×10^6	1.44×10^{-6}	1.24×10^{18}	64.5	4.56
4.0	40.00	2.56×10^6	2.90×10^2	8.34×10^5	4.71×10^{-6}	4.18×10^{16}	54.7	3.93

TABLE III Mott parameters for a-Se_{78-x}Te₂₂Bi_x, taking $\alpha = 10^7 \text{ cm}^{-1}$

X(Bi%)	A(K ^{1/4})	T ₀ (K)	R cm (243 K)	N(E _F) (eV ⁻¹ cm ⁻³)	W(m eV) (243 K)	αR
0.0	86.66	5.64×10^7	84.9×10^{-8}	3.29×10^{21}	118.63	8.49
0.5	53.33	8.09×10^6	52.3×10^{-8}	2.29×10^{22}	72.76	5.23
2.0	46.66	4.74×10^6	49.2×10^{-8}	2.92×10^{22}	65.83	4.92
4.0	40.00	2.56×10^6	39.2×10^{-8}	7.25×10^{22}	54.75	3.92

can be made is on the basis of the values of W and αR , which according to Mott and Davis [31] should be greater than kT and unity respectively for variable range hopping conduction. From the above discussion, one may conclude that at higher temperature the conduction is taking place in the extended states and at low temperatures the conduction is due to variable range hopping.

Several workers [41–43] have pointed out that, when a metal undergoes chemical combination, it forms a compound where the distribution of charge takes place in the outer level to the most likely level or surface which can be affected by the redistribution of electrons in the Fermi level or surface. That is, when a metal undergoes chemical combination and forms a compound its Fermi level should change. This can also be explained on the basis of a change in electronegativity. According to Sanderson [44], when an element combines with other elements, they come together at an intermediate value of electronegativity, which is the geometric mean of the combining atoms. In the present case we have calculated the electronegativity (X_c) of different systems using Sanderson's [44] equalization principle. From Table I we observed that the electronegativity (X_c) of the system decreases as the Bi concentration increases. So, one can infer that the decrease in density of states decreases the electronegativity of the system.

4. Conclusion

From the results and discussion as given above, it may be concluded that at higher temperature (296–390 K) the conduction in a-Se_{78-x}Te₂₂Bi_x occurs in the extended states and at lower temperature (213–296 K) the conduction is due to variable range hopping, which is in fair agreement with the Mott's condition of variable range hopping conduction. The density of states $N(E_F)$ was calculated using Mott parameters. It is observed that the calculated values of $N(E_F)$ from the above measurements decreases as concentration of Bi increases in a-Se-Te-Bi system. These results have been explained in terms of Te-Se, Bi-Se bond formation. The increase in σ_{dc} and ΔE is due to the decrease in the density of localized states.

The values of electronegativity calculated for the system decreases on adding Bi impurities. On the basis of the electronegativity of the system, it can also be concluded that the DC conductivity increases with a decrease in electronegativity which is changed by adding Bi impurities to the system.

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