D.c. conductivity and hopping mechanism in Bi$_2$O$_3$-B$_2$O$_3$ glasses

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The physical and transport properties of semiconducting glasses are highly interesting, providing useful information regarding the structure and conduction mechanism, respectively. The physical and transport properties such as density, number of ions per unit volume, hopping distance, polaron radius, d.c. conductivity and activation energy are reported. Similarly the hopping conduction mechanism is examined. The physical property (density) is used to determine the probable structure of the glass sample. The small polaron hopping model is applied to the glass system. The methods of examining the hopping conduction mechanism are discussed in the light of the small polaron model. The methods suggested by Holstein and by Sayer and Mansingh are applied to the determination of adiabatic or non-adiabatic hopping conduction. It was observed that in this system adiabatic hopping conduction is present.

1. Introduction
All glasses were treated as insulators prior to about 1955. The first reports on resistivity measurements on semiconducting glasses containing 90% V$_2$O$_5$ were presented in 1954 by Denton *et al.* [1, 2]. Since 1962, studies on electronic conduction in glasses have increased rapidly. Glasses are very interesting because of their potential applications in industry and many allied areas. After 1962 many research workers [3–6] studied glasses because of their wide range of applications such as switching and memory devices, transducers, superior insulators and dielectrics, semiconductors etc. Many kinds of components, from switching and memory diodes to computer memories, might be cheaply produced with glass. Thus glass became an ordinary electronic material [3].

The transport properties of semiconducting glasses are also highly interesting, providing useful information regarding the conduction mechanism. Ghosh and Chaudhuri [7] discussed the d.c. conductivity of semiconducting vanadium bismuth oxide glasses containing 80–95 mol % vanadium pentoxide in the temperature range 300–500 K. They observed adiabatic hopping conduction and discussed the results of measurements on the basis of a polaronic hopping model. The activation energy of electrical conduction in M$_2$O–SiO$_2$–B$_2$O$_3$ glasses containing less than 25 mol % M$_2$O (M = alkali metal) has been studied by Otto [8] observing ionic conduction. Generally the thermal activation energy for conduction appears to be a dominating factor which controls the conductivity, but in many cases the pre-exponential factor has a greater influence on conductivity [9].

At low temperature, a Mott $T^{-1/4}$ analysis was made in V$_2$O$_5$–Bi$_2$O$_3$ glasses by Ghosh and Chaudhuri [10]. According to them the polaronic models of hopping conduction can qualitatively explain the conductivity data, but fail to give a quantitative agreement. More recently, the present authors have reported the effect of annealing on the d.c. conductivity and activation energy of Li$_2$O–Al$_2$O$_3$–B$_2$O$_3$ glass [11].

In the present work, it was decided to measure the variation of d.c. electrical conductivity with temperature in the range 313 to 573 K, together with the physical properties, so as to determine the behaviour of the conduction mechanism in Bi$_2$O$_3$–B$_2$O$_3$ glasses.

2. Theory
The d.c. conductivity of semiconducting oxide glasses for the hopping of polarons in a non-adiabatic approximation is given by [12, 13].

$$\sigma = ne\mu = \frac{v_0 Ne^2 R^2}{kT} C(1 - C)\exp(-2\alpha R)$$
$$\exp(-W/kT) \qquad (1)$$

where n = number of transport ions and μ = mobility; N = number of metal ion sites per unit volume and C = ratio of ion concentration in low valence state to total concentration of metal ions; the term $\exp(-\alpha R)$ represents the electron overlap integral between sites, R = hopping distance and W = activation energy.

Assuming that a strong electron lattice interaction exists, the activation energy W is the result of polaron formation with binding energy W_p and any energy difference W_D which might exist between the initial and final sites due to variations of the local arrangements of ions. Austin and Mott [12] have shown that

$$W = W_H + (1/2)W_D \qquad \text{for } T > \Theta_D/2$$
$$W = W_D \qquad \qquad \text{for } T < \Theta_D/4 \qquad (2)$$

where W_H = polaron hopping energy, W_D = disorder energy arising from the energy difference between two neighbouring hopping sites and Θ_D = Debye temperature. The polaron hopping energy W_H is given by

$$W_H = W_P/2 \qquad (3)$$

where W_P = polaron binding energy. The polaron hopping energy W_H calculated from theory [12] is given by

$$W_H = \frac{e^2}{4\varepsilon_p}\left(\frac{1}{r_p} - \frac{1}{R}\right) \qquad (4)$$

where

$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \qquad (5)$$

ε_s and ε_∞ are the static and high-frequency dielectric constants of the glass, respectively, and ε_p is the effective dielectric constant [14]; r_p is the polaron radius, estimated from the site spacing R (for crystalline solids) [15] according to

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3} = \frac{R}{2}\left(\frac{\pi}{6}\right)^{1/3} \qquad (6)$$

Two methods have been suggested to calculate the polaron binding energy. The most general expression is given by Holstein [16]:

$$W_P = \frac{1}{2N}\sum_q |v_q|^2 \hbar\omega_q \qquad (7)$$

where $|v_q|^2$ is the electron–phonon coupling constant, ω_q is the frequency of optical phonons of wave number q and N is the site density.

Another method has been given by Mott [17] which gives a direct estimate (for polar lattices, if the distance R through which the electron must be transferred is not large compared to r_p):

$$W_P = \frac{1}{2}\left(\frac{e^2}{\varepsilon_p r_p}\right) \qquad (8)$$

In a generalized polaron model, the activation energy is

$$W = W_H - J \qquad (9)$$

where J = polaron bandwidth which is related to the electron wave function overlap on adjacent sites.

To check the nature of the hopping conduction mechanism (adiabatic or non-adiabatic), three methods have been suggested:

1. Friedman and Holstein [18] derived an expression for the mobility in the case of non-adiabatic hopping:

$$\mu = \frac{3}{2}\left(\frac{eJ^2R^2}{kT}\right)\left(\frac{\pi}{kTW_H}\right)^{1/2}, \exp(-W_H/kT) \qquad (10)$$

while E_{min} and Holstein [19] derived an expression for the mobility in the case of adiabatic hopping:

$$\mu = \frac{4}{3}\left(\frac{e\omega_0 R^2}{kT}\right)\exp[(J - W_H)/kT] \qquad (11)$$

2. In the second method, the polaron bandwidth J should satisfy the inequality suggested by Holstein [16]:

$$J > \left(\frac{2kTW_H}{\pi}\right)^{1/4}\left(\frac{\hbar\omega_0}{\pi}\right)^{1/2} \quad \text{Adiabatic hopping}$$

$$J < J^* \quad \text{Non-adiabatic hopping} \qquad (12)$$

The polaron bandwidth J can be estimated from

$$J \simeq e^3 [N(E_F)]^{1/2}/\varepsilon_p^{3/2} \qquad (13)$$

where $N(E_F)$ is the density of states at the Fermi level, or J can be estimated from

$$J \propto \exp(-\alpha R)$$

or

$$J = J_0 \exp(-\alpha R) \qquad (14)$$

3. The third method has been suggested by Sayer and Mansingh [20] and Murawski et al. [21]. When the overlap integral between sites $J_0 \exp(-\alpha R)$ approaches J_0, i.e. $\exp(-\alpha R) \to 1$, the hopping is adiabatic and it is mainly controlled by the activation energy. The d.c. conductivity is given by

$$\sigma = \frac{v_0 Ne^2 R^2}{kT} C(1 - C)\exp(-W/kT) \qquad (15)$$

To explore the nature of hopping conduction, a plot of log σ against activation energy W at a fixed temperature for glasses of different compositions is to be plotted. If this plot shows a straight line nature, then it indicates that Equation 15 is valid. This plot gives a slope equal to $1/kT$ and the intercept on the log σ axis gives the value of the constant A, where $A = \log [(v_0 Ne^2 R^2/kT) C(1 - C)]$.

From the slope of the plot of log σ versus activation energy, $1/kT$, the value of the temperature is estimated. If the estimated temperature is found to be nearly equal to the observed temperature, then the hopping conduction is adiabatic in nature and it is mainly controlled by the activation energy. If Equation 15 is not valid the value of estimated temperature from the plot and the fixed temperature observed will be very different; this will then suggest that the nature of hopping conduction is non-adiabatic.

3. Experimental procedure
3.1. Sample preparation and characterization
The glasses of Bi_2O_3–B_2O_3 were prepared from AnalaR grade chemicals by making up appropriate molar compositions. Appropriate amounts of the different chemicals in powder form were weighed on a K-ROY monopan balance having an accuracy of $\pm$ 10 µg. Homogenization of the appropriate mixtures of the components of chemicals was effected by repeated grinding. The homogeneous mixture was then placed in a fireclay crucible and was placed in a furnace. Melting was carried out in controlled conditions at temperature ranging from 1000 to 1500 $\pm$ 10 °C.

The duration of melting was generally 2 h. The homogenized molten glasses were quenched at 200 °C

in a steel disc so as to avoid cracking and shattering of the glass. All the samples were then immediately transferred to the annealing furnace. All the samples were annealed at 350 °C for 2 h for the removal of air bubbles or cavities formed by sudden quenching. All glasses after annealing were subjected to finishing processes such as cleaning and polishing.

To check the amorphous nature of glass samples, X-ray diffraction (XRD) patterns were taken on a Philips X-ray diffractometer PW1730. It was observed that all the samples were amorphous in nature.

The densities of glass samples were measured using the Archimedes principle. Benzene was used as a buoyant liquid. The accuracy in the measurement of density was $\pm$ 0.001 g cm^{-3}.

3.2. Electrical measurements

The d.c. electrical conductivity σ was measured by determining the resistance of the glass sample. The resistance of the glass samples was measured by a $10^{12}\Omega$ bridge-type circuit, developed in the laboratory by us. The voltage drop method was adopted. The voltage drop across a standard resistance was measured by a digital multimeter DT-850 (Japan) having input an impedance of $10^9\ \Omega$. A detailed circuit diagram is reported elsewhere [22]. The error in the resistance measurement was less than 2%.

The high-frequency dielectric constant was measured by a Marconi (UK) JA277/140 bridge, at 25 MHz at room temperature (303 K).

4. Results and discussion

The various physical properties of all the glass samples studied here, such as density, number of ions per unit volume, hopping distance and polaron radius are reported in Table I. The density is increased from 3.372 to 7.701 g cm^{-3} with the increase in Bi$_2$O$_3$, and is found to be of the same order as borate glasses in general [23]. The structure of the glass depends on the nature of ions entering the network and hence the density of the glass. As the molar percentage of Bi$_2$O$_3$ increases the density of glass sample increases. At high temperature Bi$_2$O$_3$ forms a regular Bi$_4$O$_6$ molecular lattice. The Bi$_4$O$_6$ molecules are, however, not isolated but are connected by means of their oxygen atoms in such a way that bismuth attains the coordination

number 6 with an octahedral grouping of oxygen atoms [24]. Addition of Bi$_2$O$_3$ to B$_2$O$_3$ increases the number of non-bridging oxygen atoms. This increases the density of the glass.

The concentration of ions is found to be of the order of 10^{22} cm^{-3}, and these ions decreased with the percentage increase in the composition of Bi$_2$O$_3$.

The value of the polaron radius is found to be around 0.17 nm, suggesting the formation of small polarons.

The d.c.-conductivity (σ) is measured in the temperature range 313 to 573 K. The value of d.c. electrical conductivity is found to be of the order of 10^{-11} to $10^{-14}\ \Omega^{-1}$ cm^{-1} at 313 K. It is observed that the plot of $-\log \sigma$ versus $1/T$ shows a non-linear nature (Fig. 1) and the conductivity of the glass sample increases with a rise in temperature. The slope of the curve increases towards the higher temperatures. This
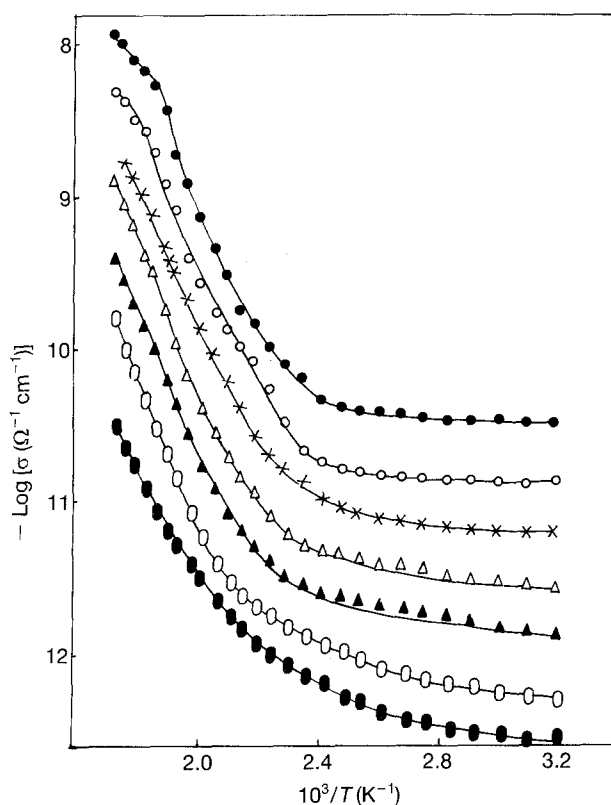

Figure 1 D.c. conductivity ($-\log \sigma$) versus $1/T$ for the samples ($\bullet$) YX1, ($\bigcirc$) YX2, (X) YX3, ($\triangle$) YX4, ($\blacktriangle$) YX5, ($\mathbf{0}$) YX6 and ($\bullet$) YX7 in the temperature range 313 to 573 K.

TABLE I Physical parameters of Bi$_2$O$_3$–B$_2$O$_3$ glasses

Glass No.	Chemical Composition Bi$_2$O$_3$–B$_2$O$_3$	Density (gm cm^{-3})		Concentration of ions (10^{22} ions cm^{-3})	Hopping distance (nm)	Polaron radius r_p (nm)
		d_{theo}	d_{expt}			
YX1	20–80	3.22	3.372	1.42	0.412	0.166
YX2	30–70	3.93	4.010	1.31	0.423	0.170
YX3	40–60	4.64	4.544	1.22	0.433	0.174
YX4	50–50	5.35	5.273	1.20	0.436	0.175
YX5	60–40	6.06	5.977	1.18	0.439	0.176
YX6	70–30	6.77	6.705	1.15	0.442	0.178
YX7	80–20	7.48	7.701	1.12	0.446	0.180

TABLE II Transport properties of Bi_2O_3-B_2O_3 glasses

Glass No.	Polaron binding energy, (eV) W_p	Polaron hopping energy, (eV) W_H	Polaron bandwidth (eV)		Effective dielectric constant,[a] ε_p	Density of states at Fermi level, (eV^{-1}) cm^{-3}) × 10^{-22} $N (E_F)$
			J	J [15]		
YX1	0.834	0.417	0.348	0.033	3.1	4.94
YX2	0.767	0.383	0.314	0.032	3.3	4.05
YX3	0.825	0.412	0.343	0.032	3.0	3.38
YX4	0.848	0.424	0.355	0.032	2.9	3.02
YX5	0.700	0.350	0.281	0.030	3.5	2.72
YX6	0.710	0.355	0.286	0.029	3.4	2.28

[a] $\varepsilon_p \simeq \varepsilon_\infty$, where ε_∞ = high (infinite) frequency dielectric constant (here at 25 MHz frequency).
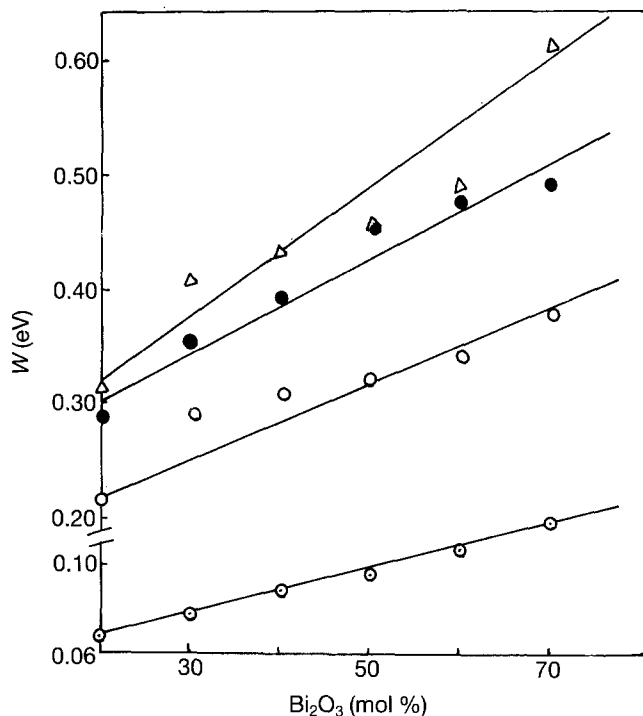

Figure 2 Variation of activation energy with composition (mol % Bi_2O_3) for various temperatures: (⊙) 403 K, (○) 443 K, (●) 513 K, (△) 533 K.

Figure 3 D.l. conductivity (-log σ) versus activation energy at the temperature 403 K. The estimated temperature from the slope of this plot is 393 K

shows that the electric conduction is electronic in nature. From the slope of the plot of − log σ versus $1/T$, the activation energy is estimated at a given temperature; because of the non-linear nature of the plot (Fig. 1) the activation energy is temperature-dependent. The d.c. electrical conductivity of glass samples is found to increase with the increase in percentage of Bi_2O_3.

Fig. 2 shows the plot of activation energy versus composition (mol% Bi_2O_3) at different temperatures (403, 443, 513 and 533 K). It is observed that as the percentage of Bi_2O_3 increases the activation energy of electrical conduction increases, in a linear manner. Similarly the activation energy also increases with the increase in temperature.

To examine the nature of hopping conduction (adiabatic or non-adiabatic), the condition given by Holstein [16] is applied. He has suggested that the polaron bandwidth J should satisfy the inequality of Equation 12. Accordingly the values of J (from Equa-
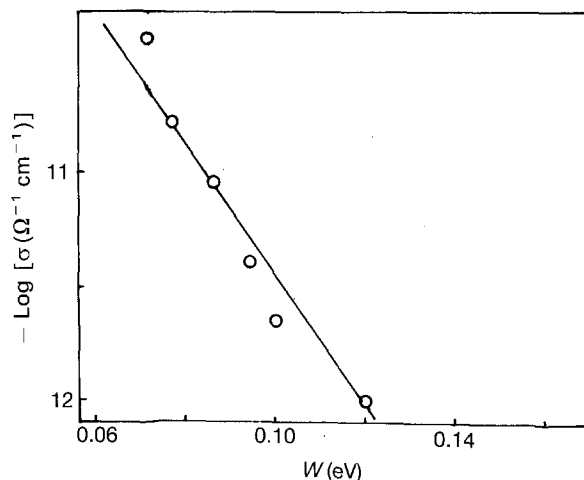
tion 9) and J^* (from Equation 12, right-hand side) are calculated (Table II). The values of J for all the glass samples studied here are greater than the value of J^*, suggesting that the nature of hopping conduction is adiabatic in nature.

Similarly, to confirm the nature of hopping conduction another method suggested by Sayer and Mansingh [20] and Murawski et al. [21] is applied. The exploration of Equation 15 is done by plotting − log σ versus activation energy W (Fig. 3) at a fixed temperature (403 K) for glasses of different compositions. This plot shows a straight-line nature, indicates that Equation 15 is valid. From the slope of the plot the value of temperature (T) is estimated and is found to be 393 K, which is very close to the fixed temperature (403 K) chosen. This indicates that the hopping conduction is adiabatic in nature, and that it is mainly controlled by the activation energy.

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