3. TRANSPORT MECHANISM IN GLASSES

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3. Transport Mechanism in Glasses

3.1 Introduction

The physical and transport properties of glasses are of great interest because of their applications in science, industries and many allied areas. The density and molar volume are the important physical properties of glasses. The density is related to the structure of glass. The density of glass is additive and can thus be calculated on the basis of the glass composition. The structure of glass can be explained in terms of molar volume. The variation in the molar volume with the molar composition of an oxide indicates the preceding structural changes through a formation or modification process in the glass network. The transport properties of semiconducting glasses provide useful information about conduction mechanism. Glasses shows both ionic and electronic conduction. In order to find out the nature of conduction in oxide glasses the investigations were performed by several workers.

The electrical conductivity of glasses varies with composition and temperature. The high alkali content gives high conductivity. Firstly, Denton et al (1954) observed the electrical conduction in oxide glasses in 1954.

On an atomic scale, the conventional silicate based glasses are made up of relatively open but continuous network of silicon atoms each bonded tetrahedrally to oxygen atoms, in the interstices of which are situated cations i.e. Na+, Ca++. As long as 1980's it was shown that these glasses are basically ionic conductors, the electricity being carried by the comparatively mobile alkali ions, with some exceptions. Silicate and oxide glasses can be regarded as solid electrolytes in which only the cations are appreciably mobile.

The glasses are very important amorphous materials as their applications are increasing very rapidly in solid state devices. Structurally glasses are amorphous and
electrically insulators. However the electronic band structure of these disordered solids can lead to semiconductor and metal behavior under different conditions. The most useful parameter of a solid electrolyte is its ionic conductivity variation as a function of temperature. This parameter determines the mass transport rate through the solid and thus influences the power consumption of an electrochemical device, of which solid electrolyte forms a part.

There are two techniques for the measurement of conductivity.

i) **AC conductivity measurement**:

   This technique is used to identify good ionic conductors, complex impedance, admittance, permittivity and modulus are the four basic functions for analysis of AC data. Angell (1981) has studied AC response of fluroborate and sulphoborate glasses.

ii) **DC conductivity measurement**:

   This technique is used to identify good ionic as well as electronic conductors. Usually in any given compound, the contribution of ionic or electronic components to conductivity depends on the temperature range. Only in few cases both components contribute significantly in a particular range of temperature. Thus compounds can be classified as
   a) pure ionic,
   b) pure electronic and
   c) mixed conductors, where both electronic and ionic components contribute.

   The electrical conductivity can be studied as a function of temperature, frequency, composition and partial pressure. When solid electrolyte possess conductivity due to both ionic and electronic transport, it is necessary to distinguish between solids, which are relevant only to the domain of semiconductor and those deal more particularly with...
electrochemical studies. This distribution is however neither easy nor clear to establish. In some electrolytes, the ionic conductivity can disappear at low temperature and the electronic conductivity can disappear at higher temperature.

In the present chapter, the results of physical measurements, dc conductivity measurement and thermally stimulated dc conductivity measurements are presented.

3.2 Review of Literature

3.2.1 Physical properties

The physical properties such as density, molar volume etc of glasses are of great interest as they provide the information about the structure of glasses. The physical properties of glasses are depends on the method of preparation (Paul 1978, Burzo et al 1980). The results of structural investigations of various types of B_2O_3 glass with different thermal histories have been presented by Soppe et al (1988). The density and glass transition temperature depends on the rate of cooling at which the glass is quenched.

The characterization studies of potassium phosphotungstate glasses and a model of structural units are carried out by Ulgaraj et al (1989). The physical properties such as density and molar volume have been investigated. Mandal et al (1993) have studied the density and molar volume of glassy lead vanadates. The density of the glass samples decreases continuously with increase of V_2O_5 content in glass composition.

Yawale et al (1993) have studied physical and transport properties of Bi_2O_3-B_2O_3 glass system. Densities, glass transition temperature and structural models resulting from extremely modified caesium and rubidium borate glasses analysed in terms of generalized structural model for each alkali family were reported by Royal et al (1994).

The structural properties of nonconventional lead cuprate glasses have been discussed by Hazra et al (1995). The compositional dependence of density, molar volume and glass transition temperature suggests that all the glass composition in this domain have
the same topology and network connectivity. The glass structure is built up of PbO₄ tetrahedral units.

The general procedure for making glass ceramic superconductors and some of their physical properties has been discussed by Chaudhary et al (1995). All these glasses which becomes superconductors after proper annealing at higher temperatures are in general transition metal oxides with copper ions. So the usual theoretical models of polaronic hopping conduction mechanisms are valid for explaining the semiconducting behavior of these oxide glasses.

Ghosh et al (1995) have investigated the density and molar volume of non-conventional transition metal ion glasses and results shows that the density increases with the increase of PbO content. They have reported that the density of the PbO-CuO glasses is higher than that of the PbO-V₂O₅ glasses.

Ivanova et al (1997) have reported the glass forming region, density, molar volume, microhardness and glass transition temperature in chalcogenide Ge-Se-Te system. In these glasses the property-composition dependence at average co-ordination number Z equal 2.4 is attributed to the network transition from a floppy to rigid type.

The density and index of refraction of NaPO₄-ZnO glasses increases linearly in accordance with the network modifying behavior of ZnO (Montagne 1998). Blagojevic et al (1999) have observed that the substitution of ZnO for PbO or SiO₂ in the PbO-B₂O₃-SiO₂ system strongly affects the density, thermal expansion and hydrolytic durability properties of all glasses.

Thermal and substituting effects of transition metal ions (Cr³⁺ or Mn⁴⁺) on physical properties of V₂O₅-P₂O₅ glasses were studied by El-Shaarawy et al (2000). The density and molar volume of the glasses were found to be changed with the composition and the heat treatment of the glasses.
3.2.2 Dc-conductivity and thermally stimulated conductivity

Mott (1968), Austin (1969), and Owen (1970) have given the information regarding the conduction process in semiconducting glasses. For semiconducting behavior in glasses, in general, the transition metal ion should exit in more than one valence state. Hence conduction occurs through transfer of electrons from low to high valence state (Sayer et al 1972).

The electrical conductivity of As$_2$Se$_3$-As$_2$Te$_3$ glassy alloys has been studied by El- Mously et al (1977). The linear dependence of electrical conductivity on the inverse of temperature over the entire compositional range indicates semiconducting behavior of glassy alloys.

Ghosh et al (1984) have discussed the results of dc-conductivity of semiconducting vanadium bismuth oxide glasses, containing 80-95 mol % vanadium pentoxide in the 300-500 K temperature range on the basis of polaronic hopping model. Similarly they have observed adiabatic hopping conduction.

The electrical properties of V$_2$O$_5$-B$_2$O$_3$ glasses are discussed on the basis of small polaron hopping model by Culea et al (1986). The charge transfer mechanism plays a dominant role in semiconducting glasses. It is observed that in most of the glass system polaron hopping model fits qualitatively.

The influence of Ag$_2$SO$_4$ addition on electrical conductivity of Li$_2$O-B$_2$O system has been studied by Singh et al (1989). The enhancement of conductivity with a change in the structure of metaborate glass is reported to be due to Ag$_2$SO$_4$. The measurements of dc-conductivity of six samples of sodium-cuprous phosphate glasses having different cuprous ion concentration in the temperature range 80-490 K have been made by Singh et al (1989). The activation energy is evaluated and the possibility of ionic or electronic conduction is discussed. In Cu$^+$ ion conducting glass system it has been found that the variation of dc-conductivity with temperature follows Arrhenius relationship.
Dc-conductivity and hopping mechanism in $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ glasses has been studied by Yawale et al. (1993). The physical and transport properties such as density, number of ions per unit volume, hopping distance, polaron radius, dc-conductivity and activation energy are reported by them. The small polaron hopping model is applied to the glass system.

Dc-conductivity, density and infrared investigations have been carried out on $\text{ZnO-PbO-B}_2\text{O}_3$ glasses by Doweidar et al. (1994). The results are discussed by considering the dual role of $\text{ZnO}$ and its effect on glass structure. It is concluded that these properties are controlled by the structure of the zinc lead borate network. Transport properties (density, dc-conductivity and NMR investigation) of semiconducting $\text{Fe}_2\text{O}_3$-$\text{PbO-B}_2\text{O}_3$ glasses were studied by Doweidar et al. (1994). The dc-conductivity and the activation energy for conduction changed markedly with $\text{Fe}_2\text{O}_3$ content. The high temperature conductivities can be described by Mott’s model for the phonon-assisted hopping of small polarons. The polaron hopping is shown to be non-adiabatic. The low temperature conductivities are characterized by the variable range hopping mechanism.

Ghosh et al. (1993) have reported the electrical conductivity of different compositions of silicate glasses containing copper and vanadium in the temperature range 200-500 K. They have reported that at high temperature, Mott’s model of phonon-assisted small polaron hopping between nearest neighbour is consistent with the data, while at low temperature the variable range-hopping model appears to be valid.

Ansari et al. (1994) have reported measurements of electrical conductivity, thermoelectric power and dielectric constant of $\text{ZnMoO}_4$ sample over an extensive range of temperature (300-1250K). They found that, the compound is n-type semiconductor with energy band gap 2.94 eV. Yawale et al. (1994) have studied the dc-electrical conductivity of $\text{V}_2\text{O}_5$-$\text{ZnO-P}_2\text{O}_5$ semiconducting glasses over a composition 50-70 (mol %) $\text{V}_2\text{O}_5$ in the
temperature range 307-475K. Log $\sigma$ Versus 1/T plot exhibits linearity. The nature of hopping conduction is studied from linearity of log $\sigma$ versus activation energy ($\Delta E$) at fixed temperature. Adiabatic hopping conduction is observed.

Wasiucionek et al (1994) have measured electrical properties of three series of glasses of Na$_2$O-V$_2$O$_5$-P$_2$O$_5$ system corresponding to different V$_2$O$_5$, P$_2$O$_5$ ratios. Each series consisted of samples of various sodium contents. A mixed ionic electronic conductivity is observed.

Electrical conduction in both single and mixed alkali tellurite glasses is satisfactorily explained by the interchange transport mechanism based on the site-memory effect exhibited by the glass network (Sunandana 1995). In TeO$_2$-B$_2$O$_3$ glass system both the conductivity and activation energy were found to be a function of added oxide type (Sabry et al 1995). Mori et al (1995) have measured dc-electrical conductivity of V$_2$O$_5$-ZnO-TeO$_2$ under Ar and O$_2$ gas atmosphere and gas sensing properties have been investigated at temperature ranging from 303 to 473 K. They concluded that telluride glass has a potential applicability to O$_2$ gas sensor.

Jayasingha et al (1995) have studied electrical properties of TeO$_2$ glasses with Na$_2$O as network modifier. Conductivity data obey an Arrhenius type behavior with some pre-exponential term in agreement with an interstitial mechanism for ion transport.

Dhote et al (1997) have examined the transport properties of Zinc-bismuth oxide glasses. They observed that, the density of Fermi level and the density of localized states are closed to each other. Gawande et al (1997) have reported the results of measurement of dc-electrical conductivity and the activation energy of CuO-Bi$_2$O$_3$ glasses. Temperature dependent conductivity and non-adiabatic hopping conduction was observed in these glasses.

Ganguli et al (1999) have studied the role of PbO in lithium ion transport in Li$_2$O-PbO-B$_2$O$_3$ glasses. The presence of lead, leads to a decrease in dc-conductivity, which
is to be due increase of partial charge on the oxygen atom and to the presence of the loan pair on the Pb atom, both of these factors impede lithium ion motion.

Dc-conductivity of XCuO-(100-X) Bi$_2$O$_3$ glasses has been studied by Sreenivasu et al (2000). They have concluded that the conduction in this system is electronic in nature and arises out of adiabatic hopping of polarons. The activation energy is found to be temperature dependent.

Different glasses in the system X PbF$_2$- (1-X) [PbO; TeO$_2$] have been synthesized and investigated (El- Damrawi 2000). Addition of PbF$_2$ to the lead telluride network can increase the conductivity by increasing both carrier concentration and mobility. The random site model was proposed to explain the fluorine ion transport mechanism in the glasses.

Hong et al (1979) have measured thermally stimulated conductivity in 4Na$_2$O-96SiO$_2$ and 30PbO-70SiO$_2$ (mol %) glasses for studying alkaline ion motion in glasses. It is concluded that the high temperature background thermally stimulated polarization current is shown to be due to the dc-conductivity.

Catchings (1981) has measured ionic conductivity of ternary sodium borosilicate glasses by thermally stimulated current method. The activation energy and pre-exponential factor, determined from dc-conductivity measurements are studied as a function of the glass composition and fraction of BO$_4$ and asymmetric BO$_3$ units as determined from the present structural model for this glass system.

The thermally stimulated polarization and depolarization current techniques were used to investigate alkali ion motion in silicate glass by Agarwal et al (1982). The TSDC peaks were observed in these glasses along with dc-conduction current at high temperatures.

Hong et al (1981) have investigated sodium ion motion in three sodium silicate glasses and a sodium aluminosilicate glass by thermally stimulated polarization...
depolarization current techniques. The high temperature background current corresponds to the sodium motion for dc-conductivity and diffusion. The commonly observed dc absorption current which was found to be related to the two TSDC peaks.

Thermally stimulated polarization and depolarization in bulk glasses of Na$_2$O-2SiO$_2$ and Na$_2$O - 3SiO$_2$ studies have been carried out by Doi (1983). It was concluded that the great reduction in dc-conductivity down to a few hundredth with decreasing sample thickness is due to the presence of inherent microheterogeneity in the glass structure.

The dc-electrical conductivity and thermally stimulated conductivity studies in lead borate glasses have been made by Sawarkar et al (1997). The dc-conductivity of thermoelectrets prepared at various polarizing temperatures and fixed polarizing field was measured. The values of activation energies and knee temperatures were reported.

Mogus-Malankoric et al (1999) have studied thermally stimulated current and dc-conduction in calcium iron phosphate glasses.

### 3.3 Theory Of Dc-Electrical Conduction

Oxide glasses have traditionally been used as insulators. In order to know nature of conduction in oxide glasses, the investigation was carried out by Warburg (1984). He established the ionic nature of conduction by demonstrating the sodium ion transport between two amalgam electrodes separated by a glass membrane. Electronic conduction in oxide glasses was observed first by Denton et al (1954). This led to the development and study of different oxide glass system showing semiconducting behaviour (Murawski et al 1979).

#### 3.3.1 Ionic conduction

In the last decade, the study of ionic conductivity of glasses has assumed importance because of the possibility of exploiting super ionically conducting glasses as...
solid electrolytes in high energy density batteries. The fast ion conducting glasses are characterized by room temperature conductivity in the range $10^{-5}$ to $10^{-2}$ (ohm-cm)$^{-1}$ and low activation energies. Ion transport in glasses has, in general been explained on the basis of a hopping mechanism, the ionic species jumping over an activation barrier ($\phi$) to contribute electrical conduction.

Stevels (1957) used this model to derive the following expression for resistivity

$$\rho = \frac{\sigma kT}{n\nu\xi^2 e^2} \exp \left( \frac{\phi}{kT} \right)$$

(3.1)

Where, $n$ is the concentration of the mobile ions, $Z_e$ is the charge of the ion, $k$ is the Boltzman constant, $\nu$ is the vibrational frequency of ion, $\xi$ is the average distance between the two sites over which jumps occur and $S$ is the number of available alternative sites to which the mobile ion may jump.

Assuming that, ionic motion occurs by filled enhanced thermally activated hopping between equivalent sites in the lattice, Elliot (1984) has derived following simple expression for ionic conductivity.

$$\sigma = \frac{Ne^2 R^2 \nu}{kT} \exp \left( \frac{-W}{kT} \right)$$

(3.2)

Where,

$N$ is the number of available ions per unit volume,
$
u$ is the vibrational frequency for an atom constrained in the potential well at a site,
$e$ is the charge on ion and
$R$ is the site spacing.
To find fast ion conduction in glasses, two theories have been put forwarded. In the random site model (Glass 1980) all ions of particular type are assumed to be potential charge carriers. Thus the mobility in such glasses should vary with glass composition. In weak electrolyte model, only a fraction of ions of the relevant variety contributes to the electrical conductivity. The mobility in such a system is independent of glass composition (Ravaine et al 1977).

3.3.2 Conduction mechanism in amorphous semiconductors

There are glassy materials exhibiting electronic conduction. Glasses can be classified according to variety of criteria on the basis of composition. They are classified as oxide glass semiconductors and chalcogenide glass semiconductors.

The electrical conductivity of oxide glasses depends upon the following factors.

I) Ratio of high/low valence ions
II) Concentration of transition metal oxide
III) Contribution of ionic and/or electronic conductivity
IV) Hopping distance of the transition metal ions
V) Melting temperature of the glass system
VI) Annealing time and annealing temperature of the glass system (Hamblen et al 1963).
VII) Environment may also affect the conductivity of the glass sample (especially at high temperature, because the valence ratio changes with temperature).

In amorphous semiconductors, conduction occurs generally through charge transfer mechanism called hopping conduction.

The electron density \( n(w) \) at any particular energy from the Fermi-Dirac Probability can be written as (Le Comber 1979).

\[
n(W) = g(W) f(W) \tag{3.3}
\]
Where,

\[ f(W) = \frac{1}{[1 + \exp\left(\frac{W - W_p}{kT}\right)]} \]  (3.4)

is the Fermi-Dirac Probability. \( W_p \) is the Fermi energy. But for energies more than few kT away from \( W_p \), we approximate equation (3.4) to its classical Maxwell-Boltzman form. So,

\[ n(W) = g(W) \exp\left[-\frac{(W - W_p)}{kT}\right] \]  (3.5)

We know that, the conductivity \( (\sigma) \) is given by

\[ \sigma = n(W) \mu e \]

or

\[ \sigma = e \mu g(W) \exp\left[-\frac{(W - W_p)}{kT}\right] \]  (3.6)

Similarly, we can write expression for hole concentration also. It is observed from equation (3.6) that conductivity depends upon mobility \( (\mu) \) of the charge carriers.

Consider first the extended state \( W \) in fig. (3.1). At the energies into conduction band i.e. \( W >> W_c \), the mobility is expected to be similar to that in crystal. But these energy states do not make any significant contribution to conductivity. As \( W \) approaches \( W_c \), the disorder in lattice increases the scattering. Therefore under these conditions the electron transport may no longer be considered. According to Cohen (1970), the conduction process is similar to Brownian motion.

The electron can jump from site to site without the need of thermal activation in the normal hopping. The motion of electron jump above \( W_c \) is taken into consideration.
According to random phase model (Spear et al. 1975, 1976)

\[
\mu (W) = \frac{2\pi ea^5 Z J^2 g(W)}{3 \hbar kT}
\]

\[\text{(3.7)}\]

Where,

- \(J\) is electron transfer integral between nearest neighbours,
- \(a\) is the distance of separation and
- \(Z\) is co-ordination number of particular lattice.

On combining equations (3.6) and (3.7), we get

\[
\sigma (W) = \sigma_0 (W) \exp \left[-\frac{(W_c-W_p)}{kT}\right]
\]

\[\text{(3.8)}\]

In amorphous materials sudden transition from extended to localized states at \(W_c\).
has importance so as to understand the conductivity. Therefore, we would not expect same
transport process in these levels. The nature of transport through these localized gap states
occurs through hopping process.

According to Mott (1969), at low temperatures when electron hops to a
different distance R, other than the normal hopping distance, it needs to gain an energy W,
from the lattice. Lower the temperature, it will hop to a greater distance to find a site at
lower energy W. This process of hopping is called variable range hopping. The expression
for the conductivity in low temperature region is given by

$$\sigma = \sigma_0 \exp \left[-\frac{T_0}{T}\right]^{\frac{1}{4}}$$  (3.9)

Where $\sigma_0$ and $T_0$ are parameters involving $g(W)$.

Various models for conductivity have been suggested such as polaron
hopping model, variable range hopping, hopping transport under alternating current,
polaron activated hopping, compensation model etc. Out of these only polaron hopping
and variable range models are discussed in details.

3.3.3 Polaron hopping model

This model has been suggested by Austin et al (1969), giving detailed theory
and the formulae for the evaluation of various parameters such as conductivity, activation
energy pre-exponential factor etc. The temperature dependence of dc-electrical
conductivity is discussed.

A charge carrier in a given state will always distort its surrounding. The distor-
tion will tend to lower the energy of the carrier and in extreme cases will lead to the carrier
being self trapped by the distortion and a polaron is formed (Elliott 1983). The idea of
polaron formation is described by assuming electron cloud surrounded by the charged
particles. Due to polaron formation, the hopping between nearest neighbors starts. This process is called charge transfer mechanism. This charge transfer mechanism is responsible for the electronic conduction in glasses.

The mobility ($\mu$) in hopping process is given by (Mott 1969)

$$\mu = \frac{v e R^2}{kT} \quad (3.10)$$

Where,

- $R$ is the jump distance between the sites or hopping distance,
- $v$ is the hopping frequency and
- $k$ is Boltzmann constant

The hopping probability $P$ may be written as (Mott et al 1971)

$$P = \exp(-2\alpha R) \exp(-W/kT) \quad (3.11)$$

The jump frequency $v$ can be written as

$$v = v_0 \exp(-2\alpha R) \exp(-W/kT) \quad (3.12)$$

and is of the order of phonon frequency ($10^{12}$ to $10^{13}$ Hz) and

$$\alpha = \frac{(2m W)}{\hbar^2} \frac{1}{\alpha}$$

is the tunneling probability.

The dc-conductivity of semiconducting oxide glasses for the hopping of polarons in non-adiabatic approximation is given by (Mott 1968 and Austin et al 1969).

$$\sigma = Ne\mu = \frac{v N e^2 R^2}{kT} C (1-C) \exp(-2\alpha R) \exp\left(-\frac{W}{kT}\right) \quad (3.13)$$
Where,

\( V \) is the phonon frequency,
\( N \) is the number of transition metal ion sites per unit volume,
\( R \) is the average hopping distance,
\( C \) is the ratio of the ion concentration in the low valence state to the total concentration of transition metal ions,
\( \alpha \) is the electron wave function decay constant so that \( \exp(-2\alpha R) \) represents electron overlap integral between sites and
\( W \) is the activation energy arising from the electron-lattice interaction.

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 \( W^\circ \) which might exits between the initial and final sites due to variations of the local arrangement of ions. Austin et al. (1969) have shown that

\[
W = W_H + (1/2) W_D \quad \text{for } T > \theta_D / 2
\]
\[= W_D \quad \text{for } T < \theta_D / 4
\]

Where,

\( W_H \) is the polaron hopping energy,
\( W_D \) is the disorder energy arising from the energy difference between the neighbouring hopping sites and
\( \theta_D \) is the Debye temperature.

A value of Debye temperature is given by

\[
\theta_D = \frac{h \nu}{k}
\]
The polaron hopping energy, $W_{hi}$ is given by

$$W_{hi} = W_p / 2 \quad (3.16)$$

Where $W_p$ is the polaron binding energy.

The polaron hopping energy, $W_{hi}$ calculated from theory (Austin et al. 1969) is given by,

$$W_{hi} = \frac{e^2}{4 \varepsilon_p} \left( \frac{1}{r_p} - \frac{1}{R} \right) \quad (3.17)$$

Where,

$$1/\varepsilon_p = 1/\varepsilon_\infty - 1/\varepsilon_s \quad (3.18)$$

$\varepsilon_s$ and $\varepsilon_\infty$ are the static and high frequency dielectric constants of the glass respectively. $\varepsilon_p$ is an effective dielectric constant (Bogomolov et al. 1967), $r_p$ is the polaron radius, which is estimated from the site spacing $R$ (for the crystalline solids) (Bogomolov 1968) given by,

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N'} \right)^{1/3} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} = \left( \frac{R}{2} \right) \left( \frac{\pi}{6} \right)^{1/3} \quad (3.19)$$

To calculate polaron binding energy ($W_p$), two methods have been suggested. The most general expression is given by Holstein (1959).

$$W_p = \frac{1}{2N'} \sum_q \left| v_q \right|^2 \omega_q \quad (3.20)$$

Where $\left| v_q \right|^2$ is the electron-phonon coupling constant, $\omega_q$ is the frequency of optical phonons of wave number $q$ and $N'$ is the site density.
Another method has been given by Mott (1969) which gives direct estimate (for polar lattices, if the distance $R$ through which the electron must be transferred is not large compared to $r_p$).

$$W_p = \frac{e^2}{2\varepsilon_p r_p} \quad (3.21)$$

In generalized polaron model, the activation energy

$$W = W_H - J \quad (3.22)$$

Where,

$J$ is polaron bandwidth, which is related to the electron wave function overlap on adjacent-sites.

In order to check the nature of hopping conduction mechanism (adiabatic or non-adiabatic) following three methods have been suggested.

i) Friedman and Holstein (1963) derived an expression for the mobility in case of non-adiabatic hopping,

$$\mu = \left( \frac{3e J^2 R^2}{2kT} \right) \left( \frac{\pi}{kT W_H} \right)^{1/2} \exp \left( \frac{-W_H}{kT} \right) \quad (3.23)$$

While Emin and Holstein (1969) derived an expression for the mobility in case of adiabatic hopping.

$$\mu = \frac{4e \omega_c R^2}{3kT} \exp \left( \frac{J-W_H}{kT} \right) \quad (3.24)$$

ii) In the second method, the polaron bandwidth $J$ should satisfy the inequality suggested by Holstein (1959)
$J \gtrsim \left( \frac{2kT W_h}{\pi} \right)^{1/4} \left( \frac{\hbar \omega}{\pi} \right)^{1/2}$ \hspace{1cm} (3.25)

$> \text{ for adiabatic hopping}$ \hspace{1cm} $\gtrsim J^*$

$< \text{ for non-adiabatic hopping}$

Where,

$$J^* = \left( \frac{2kT W_h}{\pi} \right)^{1/4} \left( \frac{\hbar \omega}{\pi} \right)^{1/2}$$ \hspace{1cm} (3.26a)

The polaron bandwidth $J$ can be estimated from

$$J = \frac{e^3 [N(E_p)]^{1/2}}{\varepsilon_p^{3/2}}$$ \hspace{1cm} (3.26b)

Where $N(E_p)$ is the density of states at Fermi level.

or $J$ can be estimated from

$$J \propto \exp(-\alpha R)$$ \hspace{1cm} (3.27)

or

$$J = J_o \exp(-\alpha R)$$ \hspace{1cm} (3.28)

iii) The third method has been suggested by Sayer \textit{et al} (1972) and Murawski \textit{et al} (1979).

When the overlap integral between sites $J_o \exp(-\alpha R)$ approaches $J_o$ i.e. $
\exp(-\alpha R) \rightarrow \text{unity}$, the hopping is adiabatic and it is mainly controlled by the activation energy.
The dc-electrical conductivity is given by

\[ \sigma = \frac{v N e^2 R^2 C (1-C)}{kT} \exp\left(\frac{-W}{kT}\right) \]  \hspace{1cm} (3.29)

To explore the nature of hopping conduction, graph of log \( \sigma \) 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 (3.29) is valid. This plot gives a slope equal to \( 1/kT \) and the intercept on the log \( \sigma \) axis gives the value of the constant \( A \).

Where

\[ A = \log\left(\frac{v N e^2 R^2}{kT}\right) C (1-C) \]  \hspace{1cm} (3.30)

From the slope of the plot of log\( \sigma \) 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 activation energy. If equation (3.29) is not valid, the value of estimated temperature observed will be very different, this will then suggest that the nature of hopping conduction is non-adiabatic.

### 3.3.4 Variable range hopping

This model has been suggested by Mott \textit{et al} (1979). A degenerate gas in highly disordered medium is considered. The behavior of dc-conductivity is observed when the Fermi energy lies in the range of energies when states are localized. The two possible mechanisms for conductivity are discussed viz.

I) Excitation of electrons to the conduction band energy. This type of conduction
normally occurs at high temperature.

II) Thermally activated hopping conduction by electrons in states near Fermi energy.

If localization is very strong, an electron normally jumps to the state nearest in space because the term $\exp(-2\alpha R)$ falls off rapidly with distance. This is called nearest neighbor hopping (Miller and Abrahams 1960). This type of hopping is only expected if $\alpha R_o >> 1$, where $R_o$ is the average distance to a nearest neighbor.

At sufficiently low temperature ($T < \theta_b / 4$) or if $\alpha R_o$ is comparable with or less than unity, the phenomenon of variable range hopping is always to be expected. The hopping distance $R$ increases with decreasing temperature. This was first pointed out by Mott (1968, 1969). We consider that at temperature $T$, the electron will normally hop to a site at a distance smaller than a value $R$ which depends on the temperature. This implies that it will have available $(4\pi/3) \left( R/a \right)^3$ sites. It will normally jump to a site for which the activation energy $W$ is as low as possible and for this site, the expression for the conductivity is given by

$$\sigma = B \exp \left(-A / T^{1/4}\right)$$

(3.31)

Where,

$$A = 4 \left( \frac{2\alpha^3}{9\pi k N(E_p)} \right)^{1/4}$$

(3.32)

and

$$B = \left( \frac{e^2}{2(8\pi)^{3/2}} \right) v_o \left( \frac{N(E_p)}{\alpha kT} \right)^{1/2}$$

(3.33)

Where, $N(E_p)$ is the density of states at Fermi level. $A$ and $B$ are obtained from the transport mechanism in glasses... 71.
slopes of log $\sigma$ versus $T^{-1/4}$ plot.

The mean hopping distance in VRH, $R_{\text{VRH}}$, and hopping site energy

$(W_0 = W_{\text{ph}})$ are given by

$$R_{\text{VRH}} = \left( \frac{9}{8\pi N(E_p) \alpha kT} \right)^{1/4}$$  \hspace{1cm} (3.34)

and

$$W_0 = \frac{3}{4\pi R_{\text{VRH}}^3 N(E_p)}$$  \hspace{1cm} (3.35)

According to Greaves (1973) law of VRH, the conductivity expression is given by

$$\sigma T^{1/2} = A' \exp\left[-B'/T^{1/4}\right]$$  \hspace{1cm} (3.36)

where $A'$ and $B'$ are constants.

The slope $B'$ of log $(\sigma T^{1/2})$ versus $T^{-1/4}$ is given by

$$B' = 2.1 \left( \frac{\alpha^3}{kN(E_p)} \right)^{1/4}$$  \hspace{1cm} (3.37)

From the equation (3.37), the value of density of states $N(E_p)$ can be calculated.

Schnakenberg (1968) has considered a more general polaron-hopping model in which an optical multi-photon process determines, the conductivity at high temperature, while at low temperatures charge carriers transport is an acoustical one phonon-assisted hopping process. The temperature dependence of the conductivity in this model has the form,
This equation predicts a temperature dependent hopping energy.

Recently Triberis and Friedmann (1985) have applied percolation theory to the small polaron hopping regime and evaluated the conductivity in the disordered system. Considering correlation due to energy of common sites in a percolation cluster, the following expression for the conductivity has been obtained.

\[ \sigma = \sigma' \exp\left(\frac{-\beta' T}{\beta'}\right) \]

Where \( \sigma' \) and \( \beta' \) are constant and \( \beta' \) is given by

\[ \beta' = 12.5 \alpha^3 / k N_o \]

Where \( N_o \) is the density of localized states assumed constant.

3.4 Experimental Methods

3.4.1 Measurement of physical properties

a) Density (\( d_{\text{exp}} \))

The density of glass samples was measured by Archimede's principle. Xylene was used as a buoyant liquid. The density of xylene at 303 K is 0.860 g/cc. The weight of the glass sample in air and in xylene at 303K was taken on K – Roy monopan balance having sensitivity of \( \pm 0.00001 \text{gm} \). All readings were taken at room temperature (303 K). The density was calculated using the formula.

\[ d_{\text{exp}} = \left[ \frac{a}{a-b} \right] \times 0.860 \]

\[ \left( \frac{\text{Equation 3.41}}{\text{Trans}} \right) \]
Where,
\[ d_{\text{exp}} \] is the density of the glass sample,
\[ a \] is the weight of the glass sample in air,
\[ b \] is the weight of the glass sample in xylene.

The accuracy in the measurement of density of glass samples was \( \pm 0.001 \text{g/cc} \)

b) **Molar volume \( (V) \)**

The molar volume \( (V) \) was calculated from the molecular weight \( (M) \) and density of corresponding glass samples. The formula used for calculating molar volume is

\[
V = \frac{M}{d_{\text{exp}}}
\]

Where,
\[ M \] is the molecular weight of glass sample and
\[ d_{\text{exp}} \] is the density of glass sample.

The values of \( d_{\text{theo}} \) were also calculated according to the additive rule given by Demkina *et al* (1960).

3.4.2 **Furnace and sample holder**

3.4.2 (a) **Furnace**

The furnace used for the measurement was fabricated in the laboratory. Grooved fire clay pipe was used as a muffle and 1.5 KW super kanthal wire as a heating element. A sufficient thermal insulation and shielding was done by ceramic wool. The heating rate of the furnace was controlled by the voltage supplied through dimmerstat. The digital thermometer [Shriji Electronics, 221-P (Cr/Al)] was used to record the temperature. The accuracy in the temperature measurement was \( \pm 1^\circ \text{C} \).
3.4.2 (b) Sample holder

The sample holder used for the measurements is shown in Fig. (3.2) It consists of two brass electrodes of equal area and insulator. The upper electrode is provided with a spring arrangement which helps to keep close contact between the surface of electrode and silver painted upper surface of the sample. The lower electrode is kept fixed. The electrodes are properly mounted with the help of two ceramic blocks and screws. The sample holder is kept in an earthed metal box which provides electric shielding to the sample.

![Sample holder diagram]

**Fig. 3.2**: Sample holder used for measurement

3.4.3. Measurement of dc-electrical conductivity

The dc-electrical resistance of all glass samples under study was measured by finding its resistance. The resistance of the glass sample was measured by using a voltage drop method suggested by Kher *et al* (1972) and later used successfully for glasses by Yawale *et al* (1993). The electrical circuit for dc-resistance measurement is shown in...
The circuit consists of an electronically regulated power supply and digital microvoltmeter (Systronics - 412 India) having input impedance 10 Mohm. To measure the resistance of glass sample a standard resistance \( R \) was connected in series with the glass sample. The value of standard resistance (1.053 Mohm) was verified on Aplab 4910 digital LCR-Q meter, which measures resistance up to 10 Meg ohm with an accuracy of \( \pm 0.1 \% \). The internal impedance of the source being very small, it is neglected.

Let \( R = 1.053 \text{ M ohm} \) be the standard resistance across which the voltage being measured. \( V_t \) be the total dc-voltage applied to the series combination of standard resistance \( R \) and glass sample resistance \( R_S \). Let \( I \) be the current flowing through the circuit. From fig (3.3) following equation can be obtained,

\[
\frac{V_t}{[R_S + 1.053 \text{ Mohm}]} = I
\]

Let \( V \) be the total voltage across standard resistance \( R \) (1.053 Mohm)
Then
\[
\frac{V}{[1.053 \text{ Mohm}]} = I_1
\]  \hspace{1cm} (3.44)

Since $I_1$ and $I$ are equal, we get.

\[
\frac{V}{[R_g + 1.053 \text{ Mohm}]} = \frac{V}{[1.053 \text{ Mohm}]} = I
\]

\[R_g = \left(\frac{(V_T - V)}{V}\right) \times 1.053 \text{ Mohm}\]

The accuracy of circuit is limited by tolerance of standard 1.053 Mohm resistance. The effective resistance (parallel combination of $R$ and input impedance of digital micro voltmeter) was taken into consideration while calculating the resistance of glass sample. The error in the voltage measurement due to change in voltage across standard resistance was less than 2%.

Knowing the sample resistance and dimensions of the sample, the dc-conductivity was calculated. These measurements were made in the temperature range from 303 to 553 K. The graphs are plotted between $\log \sigma$ versus $1/T$ and activation energies are calculated by finding the slope of graphs.

3.4.4 Thermoelectret preparation and measurement of thermally stimulated dc-conductivity.

a) Thermoelectret preparation

The glass samples of different compositions were mounted into the sample holder. The assembly was heated in a temperature controlled furnace to a desired polarizing temperature ($T_p$). The polarizing field ($E_p$) was maintained for 45 minutes between two
opposite faces of glass at polarization temperature ($T_p$). The sample was then cooled to a room temperature with the electric field still applied. The electric field across the sample was removed then the sample was short circuited for 10 minutes to remove the stray charges, by wrapping the sample in a conducting aluminum foil. The glass thermoelectrets were prepared by keeping polarization temperature, $T_p = 303$ K constant for each polarizing field $E_p = 1$ kV/cm, 2 kV/cm and 3 kV/cm (Sessler 1980).

The field temperature programme during changing, storage (optical) and thermally stimulated discharge is shown in Fig. 3.4.

![Field temperature programme during charging, storage (optical) and thermally stimulated discharge.](image)

b) **Measurement of thermally stimulated dc-conductivity**

The thermally stimulated conductivity of all thermoelectret prepared was measured by the same method as described in earlier section 3.4.3 (Kher et al 1972, Yawale et al 1993).
3.5 Results and Discussion

3.5.1 Physical properties

Density can be used for finding out the structure of different types of glasses. Density of glass is an additive and can thus be calculated on the basis of glass composition (Demkina et al. 1960). The structure of glass can be explained in terms of molar volume rather than the density, as the former deals with the spatial distribution of ions forming that structure. The change in molar volume with molar composition of an oxide indicates the preceding structural changes through a formation or modification process in the glass network. Winkelmann and Ann Schott (1894) proved that, the additive calculation of glass density is possible by multiplication by a suitable factor of the various oxide percentage in the glass. Hence, the glass is a mixture made up of the constituent oxides. The value of the volume of amorphous material is always higher than that for the crystalline modification of corresponding oxides (Naray-Szabo 1965). The density of the glass depends on nature, the number of ions and the way by which ions can enter the glass structure (Stevels 1957). The presence of glass former is closely related to the structure of glass in terms of spatial distribution of ions. The glass structure can also be explained in a better way in terms of molar volume. The change in the molar volume with the molar composition of an oxide suggests the change in the structure of glass through network (Sanad et al. 1985).

The experimental densities (d_{exp}) calculated by the Archimede's principle, theoretical densities (d_{theo}) calculated by additive method and molar volume for different composition of PbO mol% are reported in table (3.1). The values of d_{theo} and d_{exp} varies from 3.33 to 7.86 and 3.42 to 7.80 gm/cm$^3$ respectively. Similarly the molar volume changes from 24.68 to 29.38 cm$^3$ for glasses LB1 to LB7. The d_{theo} and d_{exp} values are found to be in close agreement with each other. This suggest that the glass structure is very much compact as like as crystal. Hence a less porosity,
vacancies and defects in the glass structure. The variation of $d_{\text{exp}}$ with lead oxide content at room temperature is shown in fig. (3.5). It is observed that the density increases linearly with increase content of PbO mol%. The variation of molar volume with lead oxide content is shown in fig (3.6). The molar volume decreases gradually with the increase in PbO mol%.

Table 3.1 Physical parameters for lead-borate glasses

<table>
<thead>
<tr>
<th>Glass no</th>
<th>Composition mol%</th>
<th>Density $d_{\text{exp}}$ (gm/cm$^3$)</th>
<th>$d_{\text{theo}}$ (gm/cm$^3$)</th>
<th>Molecular weight $M$ (gm)</th>
<th>Molar volume $V_m$ (cm$^3$)</th>
<th>Number of ions per cm$^3$ $N$ (10$^{22}$)</th>
<th>Hopping distance $R$ (Å)</th>
<th>Polaron radius $r_p$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>PbO 20  B$_2$O$_3$ 80</td>
<td>3.33</td>
<td>3.42</td>
<td>100.48</td>
<td>29.38</td>
<td>2.05</td>
<td>3.65</td>
<td>1.47</td>
</tr>
<tr>
<td>LB2</td>
<td>PbO 30  B$_2$O$_3$ 70</td>
<td>4.09</td>
<td>3.98</td>
<td>115.82</td>
<td>29.10</td>
<td>2.06</td>
<td>3.64</td>
<td>1.46</td>
</tr>
<tr>
<td>LB3</td>
<td>PbO 40  B$_2$O$_3$ 60</td>
<td>4.84</td>
<td>4.82</td>
<td>131.16</td>
<td>27.21</td>
<td>2.21</td>
<td>3.56</td>
<td>1.43</td>
</tr>
<tr>
<td>LB4</td>
<td>PbO 50  B$_2$O$_3$ 50</td>
<td>5.60</td>
<td>5.70</td>
<td>146.50</td>
<td>25.70</td>
<td>2.34</td>
<td>3.49</td>
<td>1.41</td>
</tr>
<tr>
<td>LB5</td>
<td>PbO 60  B$_2$O$_3$ 40</td>
<td>6.35</td>
<td>6.36</td>
<td>161.84</td>
<td>25.44</td>
<td>2.36</td>
<td>3.48</td>
<td>1.40</td>
</tr>
<tr>
<td>LB6</td>
<td>PbO 70  B$_2$O$_3$ 30</td>
<td>7.10</td>
<td>7.06</td>
<td>177.18</td>
<td>25.09</td>
<td>2.39</td>
<td>3.46</td>
<td>1.39</td>
</tr>
<tr>
<td>LB7</td>
<td>PbO 80  B$_2$O$_3$ 20</td>
<td>7.86</td>
<td>7.80</td>
<td>192.52</td>
<td>24.68</td>
<td>2.44</td>
<td>3.44</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Fig.: 3.5 Variation of densities with lead oxide content in lead borate glasses
It is expected, that in lead borate glasses having low proportion of lead oxide, the lead ions will exists as PbO$_2$ groups while remaining lead ions can exists as bridges between BO$_3$ and BO$_4$ groups or remain in the interstices in the glass structure. In the high lead oxide content glasses, it is expected that more easily polarizable oxygen ion could exists. The field of negative oxygen ions easily repelled the two outer electrons of the lead ion. The increase in the density with PbO mol% may be due to the loss of special symmetry of lead ions and the electron distribution towards the oxygen ions. The density and molar volume changes monotonically with composition. This indicates that, the glasses are probably in a single phase with random network structure and that the geometry and topology of the random network do not change significantly with composition (Ghosh 1995).

Fig (3.7) shows the variation of density with O/B ratio in the present glass system. The density increases linearly upto 2 oxygen to boron ratio and further increase in oxygen to boron ratio changes density slowly. Due to increase in density with increase in PbO content the number of ions per cm$^3$ taking part in conduction process also increases.
The values of different physical parameters such as number of ions per \( \text{cm}^3 \) (\( N \)), hopping distance (\( R \)) and polaron radius (\( r_p \)) obtained from density of glasses are reported in table (3.1). All these values are found to be of the order of the values reported in the literature (Ghosh et al 1986, Singh et al 1989, Yawale et al 1993).

The number of ions per \( \text{cm}^3 \) is the density of the charge carriers, found to be of the order of \( 10^{22}\text{cm}^3 \). These values calculated from physical parameters is in agreement with the value calculated from the conductivity data. This number represents the conduction process in the glass sample. It is observed that the number of ions per \( \text{cm}^3 \) increases from \( 2.05 \times 10^{22} \) to \( 2.44 \times 10^{22} \, \text{cm}^3 \) for glasses of 20 mol\% to 80 mol\% of PbO. This suggest that addition of PbO in \( \text{B}_2\text{O}_3 \) increases the concentration of ions, hence the conductivity of the glass sample. This fact is observed from the conductivity measurement of the glasses in which 80 mol\% of PbO glass shows higher conductivity than the glass of 20 mol\% of PbO.

The values of hopping distance are found to be of the order of 3.44 to 3.65 \( \text{A}^\circ \) and the polaron radius \( r_p \), 1.38 to 1.47 \( \text{A}^\circ \). Both the values are found to of the order of glasses (Singh et al 1989, Ghosh et al 1993). The value of hopping distance is...
quite resonable for the small polaron hopping. The value of polaron radius is of the order of 1.3 to 1.4 Å, indicative of small polaron formation.

3.5.2 Dc electrical conductivity

The dc-electrical conductivity of lead-borate glasses of different compositions is measured in the temperature range 303 to 553 K by measuring the resistance. It is observed that, the conductivity of glass samples studied depends on temperature and glass composition. The values of dc-conductivity are found to be of the order of $10^{12} \text{(Ohm cm)}^{-1}$ at 303 K. It is observed that, the conductivity of all the glasses studied increases with increasing temperature. The conductivity values of glasses varies from $10^{12}$ to $10^4 \text{(Ohm cm)}^{-1}$, in the temperature range, 303 to 553 K and follows the Arrhenius equation over a limited temperature range. The variation of conductivity is found to be non-linear with temperature. The values of conductivity are in good agreement with values reported by other workers (Singh et al 1989, Ghosh et al 1993, Yawale et al 1993, Sakata et al 1999, Burzo et al 1985).

The variation of dc-conductivity of lead borate glasses as a function of temperature for virgin samples is shown in fig.(3.8). The variation of conductivity with temperature is found to be systematic. The conductivity curve is divided into two linear regions called LTR (303 to 371 K) and HTR (450 to 553 K). In low temperature region (LTR), the change in the conductivity is very slow, whereas in high temperature region (HTR), the conductivity change is faster. Similar type of behaviour was observed by Marshel et al (1975), Mott et al (1979), Yawale et al (1993) and Burghate et al (1994).
Fig. 3.8 Variation of dc-conductivity of lead borate glasses with temperature (Virgin samples)
the conductivity curve is divided into two linear regions is called the kink temperature ($\theta_c$). The values of kink temperature ($\theta_c$) are reported in table (3.2) for different composition of lead borate glasses. All the glass samples studied indicates the negative temperature coefficient and a electronic conduction because no surface polarization is observed after the application of the voltage. Hence no time dependence of electrical conductivity was observed. This essentially shows that the predominant conduction is electronic. This type of behaviour is observed by Burzo et al (1985) in some lead borate glasses. They observed the two activation energies for conduction in low temperature and high temperature regions. In the present glass system, two values of activation energies are calculated at low temperature and high temperature regions. The conductivity is found to be composition dependent (fig. 3.9). The activation energies are calculated from the slope of log$\sigma$ versus 1/T plots in LTR and HTR. These values are reported in table (3.6).

The temperature at which There are four mechanisms proposed to explain conduction mechanism in glasses.

a) Carriers excited into the extended state beyond the mobility shoulders, also
called band conduction. This is operative at high temperatures.

b) Carriers excited into the localized states thermally edges also called thermally assisted tunneling which is observed between intermediate temperature range.

c) Carriers hopping between localized states near the Fermi level $E_F$ generally operative at low temperature and

d) Small polarons hopping within a dominant constituent with its associated hopping energy, which can be operative over the entire range of temperatures.

In general, it is seen that several factors such as co-ordination number of the modifier ions, character of the neighboring oxygen ligands or the state of the polarizability of oxygen anions, whether the modifier metal ion behaves as a network former or a network modifier and valence state of modifier metal ions as governed by oxidation reduction nature of glass etc, are considered to affect the conductivity of glasses. In lead borate glasses, the modifier PbO enters the glass lattice network by breaking up the random network thus introducing co-ordinated defects in the network which are nothing but simple dangling (broken) bonds. These dangling bonds may be under co-ordinated or sometimes may be over co-ordinated or floating bonds. These bonding defects give rise to electron states within the band gap of the material and these will therefore be localized in that region.

The conductivity at low temperature region can be taken due to hopping of the carriers in the localized defect states near the Fermi level. In Mott and Davis model for amorphous semiconductors, localized states of sufficiently high level exists near the center of gap, which pin Fermi level. As mentioned above, those states conceivable arise from some specific defects, characteristics of the material for e.g. dangling bonds, interstitial etc. The number of these defects will depend on the conditions of the sample preparation and subsequent annealing treatment (Mott and Davis 1971).
The variation of dc current with temperature can be attributed to ionic drift, current due to electrons hopping and current due to electrons in the conduction band. As has been stated earlier, there is a localization of structural defects in the band gap of the material. These localized states can not carry the current by themselves. The conduction involving the localized states can only take place by means of transition of electron from the filled states to neighboring empty states with phonon assistance. This type of transfer of electrons between the sites localized at different position is known as hopping which is mainly responsible for increase in the conduction with temperature. Recollecting the nature of variation of conduction with temperature in high temperature region, it can be concluded that in HTR the conduction could also be associated with small polaron hopping. The temperature dependent activation energy suggests characteristics of small polaron hopping conduction (Austin et al 1969, Mott 1968, Chung et al 1979, Ghosh et al 1991, Schnakenberg 1963 and Holstein 1959).

The experimental conductivity data in high temperature region is well described with an equation given by Mott formula (1968) eq. (3.13). With an increase in the content of PbO in glass, the conductivity increases fig.(3.9). This means a decrease in Pb-O-Pb spacing R as indicated in Table (3.1) which rises the hopping probability providing that the activation energy (W) and the fraction of reduced metal ions (C) are almost unchanged for varying composition as seen latter in small polaron hopping model. This can be seen from fig (3.10) in which the activation energy do not change significantly in LTR.

The logarithm of conductivity fig.(3.8) shows the linear temperature dependence upto a critical temperature ($\Theta_c$) and then the slope changes with deviation from linearity. Thus the activation energy is temperature dependent. Such behaviour is a feature of small polaron hopping. So the thermal variation of conductivity can be described by the small polaron hopping model based on a strong coupling of electron
with the lattice by the single phonon. This model gives the conductivity in the non-adiabatic regime by eq. (3.13).

The observed values of activation energies (W) are found to be of the order of other oxide glasses (Singh et al 1989, Ghosh et al 1993, Yawale et al 1993).

Table (3.2) reports the effective dielectric constant ($\varepsilon_p$) (which is calculated under the approximation, $\varepsilon_p = \varepsilon_{\infty}$), polaron binding energy ($W_p$) calculated from the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Glass no & Effective dielectric constant $\varepsilon_p$ & Polaron binding energy $W_p$ (eV) & Polaron hopping energy $W_H$ (eV) & Phonon frequency (v) (Hz)$10^{13}$ & Kink temperature $\theta_c$ (K) \\
\hline
LB1 & 19.7 & 0.148 & 0.0742 & 1.229 & 417 \\
LB2 & 19.0 & 0.155 & 0.0777 & 1.349 & 420 \\
LB3 & 21.4 & 0.141 & 0.0704 & 1.394 & 431 \\
LB4 & 22.0 & 0.139 & 0.0693 & 1.412 & 461 \\
LB5 & 22.1 & 0.139 & 0.0693 & 1.414 & 448 \\
LB6 & 22.7 & 0.137 & 0.0683 & 1.425 & 418 \\
LB7 & 22.9 & 0.136 & 0.0682 & 1.424 & 429 \\
\hline
\end{tabular}
\end{table}

Fig. 3.10 Dependence of activation energy (W) on composition PbO (mol%) at LTR & HTR for virgin samples.
theory of Austin et al (1969), polaron hopping energy \( W_h \), the phonon frequency \( v \) and kink temperature \( \theta_k \).

The value of effective dielectric constant \( \epsilon_p \) is calculated from infinitely high frequency dielectric constant obtained from the optical properties. It is observed that the values of \( \epsilon_p \) increases with increasing PbO mol %. The polaron binding energy \( W_p \) and the polaron hopping energy \( W_h \) are related with each other and decreases with the increasing concentration of PbO mol %. The phonon frequency is found to be of the order of \( 10^{13} \) Hz. (calculated from eq (3.26)]. The density of state \( N(E_p) \) and wave function decay constant \( (\alpha) \) values are tabulated in table 3.3(a) for low temperature region \( (337K) \) and 3.3(b) for high temperature region \( (501K) \) for virgin samples.

Table 3.3(a) Polaron bandwidth \( (J) \) and \( J^* \), density of states at fermi level \( [N(E_p)] \) and wave function decay constant \( (\alpha) \) for glass virgin samples. Temperature range \( (303 \text{ to } 371 \text{ K}) \).

<table>
<thead>
<tr>
<th>Glass no</th>
<th>Polaron bandwidth(eV)</th>
<th>Density of states ( [N(E_p)] ) eV(^{-1}\text{cm}^3 ) (From J) ( 10^{21} )</th>
<th>Wave function decay constant ( \alpha ) (A(^{-1})) ( (\text{From J}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>0.052</td>
<td>7.10</td>
<td>13.0</td>
</tr>
<tr>
<td>LB2</td>
<td>0.046</td>
<td>5.00</td>
<td>18.7</td>
</tr>
<tr>
<td>LB3</td>
<td>0.050</td>
<td>8.46</td>
<td>12.1</td>
</tr>
<tr>
<td>LB4</td>
<td>0.052</td>
<td>9.91</td>
<td>11.2</td>
</tr>
<tr>
<td>LB5</td>
<td>0.033</td>
<td>4.12</td>
<td>27.2</td>
</tr>
<tr>
<td>LB6</td>
<td>0.048</td>
<td>9.15</td>
<td>12.5</td>
</tr>
<tr>
<td>LB7</td>
<td>0.040</td>
<td>6.59</td>
<td>17.8</td>
</tr>
</tbody>
</table>
Table 3.3(b) Polaron bandwidth (J and J*), density of states at fermi level [N(Ep)] and wave function decay constant (α) for virgin glass samples. Temperature range (450 to 553 K) HTR.

<table>
<thead>
<tr>
<th>Glass no</th>
<th>Polaron bandwidth(eV)</th>
<th>Density of states [N(Ep)] eV⁻¹ cm⁻³ (From J)</th>
<th>Wave function decay constant α (Å⁻¹) (From J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J</td>
<td>J*</td>
<td></td>
</tr>
<tr>
<td>LB1</td>
<td>0.304</td>
<td>0.02766</td>
<td>2.36</td>
</tr>
<tr>
<td>LB2</td>
<td>0.250</td>
<td>0.02851</td>
<td>1.44</td>
</tr>
<tr>
<td>LB3</td>
<td>0.323</td>
<td>0.02827</td>
<td>3.43</td>
</tr>
<tr>
<td>LB4</td>
<td>0.559</td>
<td>0.02834</td>
<td>11.10</td>
</tr>
<tr>
<td>LB5</td>
<td>0.574</td>
<td>0.02836</td>
<td>11.90</td>
</tr>
<tr>
<td>LB6</td>
<td>0.410</td>
<td>0.02836</td>
<td>6.58</td>
</tr>
<tr>
<td>LB7</td>
<td>0.322</td>
<td>0.02835</td>
<td>4.18</td>
</tr>
</tbody>
</table>

The nature of hopping conduction (adiabatic or non adiabatic) is examined by the condition given by Holstein (1959). According to Holstein (1959), the polaron bandwidth J should satisfy the inequality \( J > J^* \) given by eq (3.25). Accordingly the values of J and J* are calculated and reported in table 3.3(a) and 3.3(b). The values of J for the glass samples studied are found to be greater than J*, both in high and low temperature regions, suggesting that the nature of hopping conduction is adiabatic.

In figure 3.8 it is seen that the temperature dependence of conductivity deviated from the linearity for temperature less than \( \theta_c \), above which the small polaron hopping law (SPH) is valid. An attempt is made to apply variable range hopping (VRH) in the low temperature region, less than \( \theta_c \). However the validity of such high temperature range is not beyond questions. But it has been pointed out (Mostefa et al 1992) that depending on the strength of coulomb interaction the expression for density of state at the Fermi level is modified and the VRH (Mott 1968, 1969) may be applied even at high temperature (300K) and above, though the VRH should actually be applicable in the low temperature regime below \( \theta_d / 4 \) which is
below 100K (where $\theta_D$ is Debye temperature). Therefore an attempt is made to apply both the VRH models proposed by Mott (1968, 1969) and Greaves (1973) which are valid for intermediate range of temperature. The conductivity for variable range hopping is given by the eq.(3.31). The constant A and B are obtained from slope of log $\sigma$ against $T^{-1/4}$ plot, popularly called as Mott $T^{-1/4}$ analysis (Fig. 3.11). The slope of the plot gives the values of constant A and the intercept gives the value of constant B. The values of electron wave function decay constant ($\alpha$) are considered from table 3.3 (a) for the calculation of density of states at the Fermi level $N(E_F)$. The values obtained from the log $\sigma$ versus $T^{-1/4}$ plot are reported in table (3.4). The mean hopping distance in VRH, $R_{VRH}$ and $N(E_F)$ values are given in tabel (3.4). The values of $N(E_F)$ are found to be of the order of $10^{21}$ eV$^{-1}$cm$^{-3}$. These values of $N(E_F)$ and $R_{VRH}$ are found to be reasonable for other oxide glasses (Dhawan et al 1982, Ghosh et al 1986, Mori et al 1995).

![Fig. 3.11 Plot of log of conductivity ($\sigma$) versus $T^{-1/4}$](image-url)
The another model of variable range hopping is suggested by Greaves (1973). This is applied for the intermediate range of temperature. This model demands that the \( \log(\sigma T^{1/2}) \) versus \( T^{1/4} \) plot should be linear fig. (3.12). The expression for the conductivity is given in theory section as equation (3.36). The slope of the plot yields the value of constant \( B' \) given by equation (3.37) from which \( N(E_p) \) values are estimated. The linear relationship fig. (3.12) confirms the Greaves VRH in the intermediate temperature range. The values of parameters obtained from these plots are given in table (3.5). The \( N(E_p) \) values are found to be of the order of \( 10^{21} \) eV\(^{-1}\) cm\(^{-3}\) which are found to be reasonable for usual semiconducting oxide glasses. The values of density of states \( N(E_p) \) calculated from these models are found to be in well agreement with the values reported in table (3.3a) for virgin samples. This indicates that both the models given by Mott (1968, 1969) and Greaves (1973) explains the low temperature conductivity data quantitatively and reasonably.

In general, for lead borate glasses, the high temperature conductivity data is explained by the small polaron hopping conduction and the low temperature conductivity data by the variable range hopping models suggested by

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Glass composition mol%</th>
<th>( A ) (K(^{1/4}))</th>
<th>Density of states ( N(E_p) ) (eV(^{-1})cm(^{-3})) ( \times 10^{21} )</th>
<th>Hopping distance ( R_{VRH} ) (A(^{\circ}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>PbO: 20 B(_2)O(_3): 80</td>
<td>15.66</td>
<td>7.61</td>
<td>3.33</td>
</tr>
<tr>
<td>LB2</td>
<td>PbO: 30 B(_2)O(_3): 70</td>
<td>12.85</td>
<td>50.5</td>
<td>1.84</td>
</tr>
<tr>
<td>LB3</td>
<td>PbO: 40 B(_2)O(_3): 60</td>
<td>22.85</td>
<td>1.36</td>
<td>5.22</td>
</tr>
<tr>
<td>LB4</td>
<td>PbO: 50 B(_2)O(_3): 50</td>
<td>11.23</td>
<td>18.2</td>
<td>2.78</td>
</tr>
<tr>
<td>LB5</td>
<td>PbO: 60 B(_2)O(_3): 40</td>
<td>10.29</td>
<td>3.77</td>
<td>3.31</td>
</tr>
<tr>
<td>LB6</td>
<td>PbO: 70 B(_2)O(_3): 30</td>
<td>5.55</td>
<td>4.32</td>
<td>1.22</td>
</tr>
<tr>
<td>LB7</td>
<td>PbO: 80 B(_2)O(_3): 20</td>
<td>16.66</td>
<td>15.3</td>
<td>2.59</td>
</tr>
</tbody>
</table>

The values of parameters obtained from these plots are given in table (3.5). The \( N(E_p) \) values are found to be of the order of \( 10^{21} \) eV\(^{-1}\) cm\(^{-3}\) which are found to be reasonable for usual semiconducting oxide glasses. The values of density of states \( N(E_p) \) calculated from these models are found to be in well agreement with the values reported in table (3.3a) for virgin samples. This indicates that both the models given by Mott (1968, 1969) and Greaves (1973) explains the low temperature conductivity data quantitatively and reasonably.

In general, for lead borate glasses, the high temperature conductivity data is explained by the small polaron hopping conduction and the low temperature conductivity data by the variable range hopping models suggested by
(Mott 1968, 1969) and (Greaves 1973).

![Graph showing log(σT⁻¹) versus T⁻¹ for various glass compositions.]

**Table 3.5 Greaves parameters for variable-range hopping conduction**

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Glass composition mol%</th>
<th>A (K⁻¹/²)</th>
<th>Density of states N(E_p) (eV⁻¹cm⁻³) x 10²¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>20 80</td>
<td>16.85</td>
<td>6.14</td>
</tr>
<tr>
<td>LB2</td>
<td>30 70</td>
<td>20.58</td>
<td>8.20</td>
</tr>
<tr>
<td>LB3</td>
<td>40 60</td>
<td>17.80</td>
<td>3.97</td>
</tr>
<tr>
<td>LB4</td>
<td>50 50</td>
<td>14.28</td>
<td>7.60</td>
</tr>
<tr>
<td>LB5</td>
<td>60 40</td>
<td>14.70</td>
<td>91.01</td>
</tr>
<tr>
<td>LB6</td>
<td>70 30</td>
<td>8.10</td>
<td>1.08</td>
</tr>
<tr>
<td>LB7</td>
<td>80 20</td>
<td>15.78</td>
<td>20.45</td>
</tr>
</tbody>
</table>

Fig. 3.12 Plot of log(σT⁻¹) versus T⁻¹/²
3.5.3 Thermally stimulated conductivity

The thermally stimulated conductivity of glass electrets prepared at different polarizing fields, \( E_p \) and fixed polarizing temperature \( T_p \) is measured in the temperature range 303 to 553 K. fig (3.13 a) to (3.13 g) shows variation of logarithm of conductivity \( \sigma \) with \( 1/T \) for glass electrets polarized at fixed polarizing temperature \( T_p = 303 \) K and various polarizing fields \( E_p = 1\text{kV/cm}, 2\text{kV/cm}, 3\text{kV/cm} \) and virgin sample ie. \( E_p = 0 \) kV/cm for glass electrets LB1 to LB7 respectively. From these plots, it is observed that the overall behaviour of the conductivity is same as that of the virgin glass sample. As in the previous case, the linear behaviour is observed. The conductivity curve is divided into two linear regions, which gives two values of activation energies. These values are reported in table (3.6) for low temperature and high temperature regions. This is a characteristic of small polaron hopping conduction (SPH). From the slopes of plot, the activation energies in the low and high temperature region at different polarizing fields are reported in table (3.6). It is observed that the values of activation energies in both temperature regions are found to be smaller than the virgin samples. This indicates that due to application of electric field, the charge carriers are injected into the glass bulk. This increases the charge carrier density inside the traps available originally. This can be seen from table (3.7a) and (3.7b) that the density of states at Fermi level is in general increased than the virgin glass samples. This effect is observed in conductivity of sample also, fig. (3.14) and (3.17). The plots of activation energy versus polarizing field in both the temperature regions are shown in fig (3.15) and (3.16).
Fig. 3.13(a) Variation of log of conductivity with 1/T of the glass sample LB1 polarized at fixed polarizing temperature $T_p = 303$ K and various polarizing fields $E_p = 1$ kV/cm, 2 kV/cm, 3 kV/cm and virgin.
Fig. 3.13 (b) Variation of log of conductivity with (1/T) of the glass sample LB2 polarized at fixed polarizing temperature $T_p = 303$ K and various polarizing fields $E_p = 1$ kV/cm, $2$ kV/cm, $3$ kV/cm and virgin.
Fig. 3.13(c) Variation of log of conductivity with (1/T) of the glass sample LB3 polarized at fixed polarizing temperature $T_p = 303$ K and various polarizing fields $E_p = 1$ kV/cm, 2 kV/cm, 3 kV/cm and virgin.
Fig. 3.13(d) Variation of log of conductivity with (1/T) of the glass sample LB4 polarized at fixed polarizing temperature $T_p = 303$ K and various polarizing fields $E_p = 1$ kV/cm, 2kV/cm, 3kV/cm and virgin.
Fig. 3.13 (e) Variation of log of conductivity with \((1/T)\) of the glass sample LB5 polarized at fixed polarizing temperature \(T_p = 303\) K and various polarizing fields \(E_p = 1\) kV/cm, 2 kV/cm, 3 kV/cm and virgin.
Fig. 3.13 (f) Variation of log of conductivity with (1/T) of the glass sample LB6 polarized at fixed polarizing temperature $T_p = 303$ K and various polarizing fields $E_p = 1$kV/cm, 2kV/cm, 3kV/cm and virgin
Fig. 3.13(g) Variation of log of conductivity with (1/T) of the glass sample LB7 polarized at fixed polarizing temperature $T_p = 303 \text{ K}$ and various polarizing fields $E_p = 1 \text{ kV/cm, 2kV/cm, 3kV/cm and virgin}$
Table 3.6 Activation energies ($W_L$ and $W_H$) kink temperatures ($\theta_c$) for glass samples (LB1 to LB7) polarized at fixed polarizing temperature, $T_p = 303K$ and various polarizing fields ($E_p$).

<table>
<thead>
<tr>
<th>Glass No</th>
<th>Polarizing field $E_p$ (kV/cm)</th>
<th>Activation energy $W(eV)$</th>
<th>Kink temperature $\theta_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LTR($W_L$)</td>
<td>HTR($W_H$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>303 to 371K</td>
<td>450 to 553K</td>
</tr>
<tr>
<td>LB1</td>
<td>Virgin</td>
<td>0.022</td>
<td>0.378</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.010</td>
<td>0.422</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.007</td>
<td>0.422</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.006</td>
<td>0.345</td>
</tr>
<tr>
<td>LB2</td>
<td>Virgin</td>
<td>0.031</td>
<td>0.328</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.007</td>
<td>0.338</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.036</td>
<td>0.330</td>
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<tr>
<td></td>
<td>3.0</td>
<td>0.020</td>
<td>0.302</td>
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<td>Virgin</td>
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</tr>
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<td>1.0</td>
<td>0.013</td>
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<td>2.0</td>
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<td>0.366</td>
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<tr>
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<td>3.0</td>
<td>0.033</td>
<td>0.345</td>
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<td>LB4</td>
<td>Virgin</td>
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<td>0.874</td>
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<td>Virgin</td>
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</tr>
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<td>Virgin</td>
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<td>0.525</td>
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<tr>
<td>LB7</td>
<td>Virgin</td>
<td>0.028</td>
<td>0.391</td>
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<td>0.015</td>
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<tr>
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<td>3.0</td>
<td>0.005</td>
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</table>
Table 3.7(a) Polarizing field, \((E_p)\) polaron band width \((J \text{ and } J^*)\), density of states \(N(E_p)\) and wave function decay constant \(\alpha\)  
Temperature range 303 to 371K (LTR)

<table>
<thead>
<tr>
<th>Glass No</th>
<th>Polarizing field (E_p) (kV/cm)</th>
<th>Polaron bandwidth (eV)</th>
<th>Density of states ([N(E_p)] \text{ eV}^{-1}\text{cm}^3) (From J)</th>
<th>Wave function decay constant (\alpha \text{ (A}^\circ\text{)}^4) (From J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>Virgin</td>
<td>0.0526</td>
<td>0.02519</td>
<td>7.10</td>
</tr>
<tr>
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<td>0.0646</td>
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<td>10.70</td>
</tr>
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<td>0.02519</td>
<td>11.51</td>
</tr>
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<td>0.02519</td>
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</tr>
<tr>
<td>LB2</td>
<td>Virgin</td>
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</tr>
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<td>1.0</td>
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<td>Virgin</td>
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<td>0.02582</td>
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Table 3.7(b) Polarizing field, \( (E_p) \) polaron bandwidth \( (J \text{ and } J^*) \), density of states \( N(E_p) \) and wave function decay constant \( \alpha \)

Temperature range 450 to 553 K (HTR)

<table>
<thead>
<tr>
<th>Glass No</th>
<th>Polarizing field ( E_p ) (kV/cm)</th>
<th>Polaron bandwidth(eV)</th>
<th>Density of states ( [N(E_p)] ) eV(^{-1})cm(^{-3}) (From J)</th>
<th>Wave function decay constant ( \alpha ) (A(^{-1})) ((\text{From J}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>Virgin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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</tr>
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Fig. 3.14 Variation of Log of conductivity with polarizing field \( E_p \) at HTR (523K)

Fig. 3.15 Dependence of activation energy \( W \) on polarizing field \( E_p \) at LTR (323K)
In order to observe the adiabatic and non-adiabatic conduction behaviour in the glass electrets prepared, the polaron bandwidths $J$ and $J^*$ are calculated for different polarizing fields. These values along with $N(E_p)$ and wave function decay...
constant (α) are reported in table (3.7a) and (3.7b) for LTR and HTR (303 to 371 K, 450 to 553 K respectively) for LB1 to LB7 glass electrets. It is observed that the J values are found to be greater than J*, which suggests the adiabatic hopping conduction in glass electrets.

In general, both virgin glass samples and glass electrets, the adiabatic hopping conduction is observed.

3.6 Conclusions

The values of polaron radius (r_p) for lead borate glasses are near about 1.3 to 1.4 Å, as expected for small polaron suggesting that the polaron is strongly polarized and therefore the conduction takes place by way of small polaron hopping (Singh et al 1989). In general, it is concluded that the physical parameters such as density, molecular weight, molar volume, number of ions per cm^3, hopping distance and polaron radius of glasses studied are found to be composition dependent.

The conductivity data is plotted against (1/T) for virgin and glass electrets samples. The log σ versus (1/T) plot divided into two linear regions giving two values of activation energies in LTR and HTR. This type of behaviour suggests the small polaron hopping conduction in high temperature region of all glass samples studied. The small polaron hopping conduction model explains the high temperature conductivity data is well. The low temperature conductivity data well explained by the variable range hopping model suggested by Mott and Greaves. The T^-1/4 analysis yields linear behaviour in both the models. The values of parameter obtained, density of state N(E_p) is found to be of the order of (10^21 eV^-1 cm^-3), reasonable for the semiconducting oxide glasses.

The adiabatic hopping conduction is observed in all the glasses studied. The polaron bandwidth J and J* are calculated, where values of J are found to be greater than J*. This indicates the adiabatic hopping conduction. No effect of polarizing field seems to be observed on the hopping conduction mechanism in these glasses.
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