CHAPTER V

RESULTS AND DISCUSSION OF

\((10-x)\text{SrO-xFe}_2\text{O}_3-90\text{V}_2\text{O}_5\) OXIDE GLASSES

5.1. Introduction:

An amorphous solid is a substance whose constituent particles do not have a regular or orderly arrangement. It is also known as a super cooled liquid or pseudo solid [1, 2]. Some glasses containing transition metal oxide, show semiconducting properties due to existence of transition metal ions in two different valence states such as $V^{4+}$ and $V^{5+}$. In the case of vanadium in which small polaron hopping from small valence state to a higher valence state takes place and causes electron conduction in it [3-10]. Oxide glasses doped with the transition metal oxides such as CuO, Fe$_2$O$_3$, MO$_3$, WO$_3$, V$_2$O$_5$ etc. are known to exhibit semiconducting properties [11]. The conductivity in pure transition metal ions doped glasses has always been observed to be semiconducting type because of polaron hopping between low and high valence states of transition metal ions. The polaron hopping of transition metal ions doped glasses depends on the distance between transition metal ions and their concentration. If Fe$_2$O$_3$ ions are also present along with transition metal ions, then the conductivity will be of mixed type, i.e., polaron and ionic [12].

Glasses consisting of vanadium ions play an important role in solid state chemistry and materials science. This is because of the fact that in the glass matrix with V$_2$O$_5$ pyramidal structural units. Vanadium ions, when mixed in small quantities into the glass matrices, make them useful in memory and switching
Many of the glasses having vanadium behave like semiconductors with an electrical conductivity of $10^{-3}$-$10^{-5}$ (Vcm$^{-1}$) [13]. Because of the presence of various dopant ions in the glassy host material, Glassy materials have become more promising materials exhibited quite encouraging results in their optical, electrical and magnetic properties [14, 15]. In order to understand the transport mechanism in semiconducting glasses, transition metal (TM) oxide glasses have been frequently studied from both mechanical and physical points of view [16–18]. Semiconducting glasses show lowest thermal conductivities, lowest electrical conductivity and low mobility, semiconducting chalcogenide glasses are used as raw materials. Rare earth metal oxide glasses and transition metal oxide glasses show semi conductivity due to mixed valence state [19]. Semi conductivity arises due to hopping of electron from higher valence state to lower valence state. The unpaired electron induces a polarization of the vanadium ion around it and forms a polaron. However, a more detailed modeling of the conduction process is not possible because of numerous material factors including the type and concentration of the TM ion, the number of valence states associated with the TM ion, the glass preparation conditions, and the microstructures within the glass matrix [20].

The concentration of Fe$^{3+}$ and Fe$^{2+}$ depends upon the quantitative properties of modifiers and glass formers. Iron ions are considered as effective and useful dopant ions because of the fact that they exist simultaneously in different valence states in the glass networks Fe$^{3+}$ with both tetrahedral and octahedral and as Fe$^{2+}$ octahedral coordination[21]. Fe$^{3+}$ and Fe$^{2+}$ both are paramagnetic ions; Fe$^{2+}$ ions possess a large magnetic anisotropy due tail spin orbit interaction of the 3d orbital where as such anisotropy of Fe$^{3+}$ ions is small since the anisotropic energy of Fe$^{3+}$ ions is small as the angular momentum of these ions is zero [22–24].
Glasses doped with a transition metal ion, Fe$_2$O$_3$ are used in electrochemical, electronic and electro-optic devices [25]. Sound investigations were carried out previously on the environment of iron ion in various inorganic glassy stems viz; silicate, borate, phosphate and telluride glasses [26–29]. The structural and electronic (as well as optical, magnetic and mechanical) properties of these glasses depend on the relative proportion of different valence states of the TM ions. In order to account for the effect of these valence states on the structure and properties of these glasses, it is important to control and measure the ratios of the ion concentration in the different valence states of these TM ions. Electrical switching or negative resistance phenomenon in amorphous semiconducting glasses is a very interesting study because it has a wide variety of applications such as, in power control, in information storage and in electronic and optoelectronic devices [30,31]. Extensive studies have been carried out on semiconducting oxide glasses containing transition metal ions owing to interests in their conduction mechanism and glass structure [32-38]. The mechanism of electrical conduction on semiconducting oxide glasses has generally been understood in the light of the small polaron hopping (SPH) model [39]. The semiconducting transition metal oxide glasses are important for their potential application such as optical switching and memory devices, cathode materials in batteries, electrical and switching device etc. [40–44]. The aim of the present work is to study the physical, electrical and optical properties of SrO-Fe$_2$O$_3$-V$_2$O$_5$ glass.

5.2. Experimental

Sample preparation

The glass samples having a composition (10-x) SrO - x.Fe$_2$O$_3$- 90 V$_2$O$_5$, where, x = 0, 2, 4, 6 and 8 mole % was prepared by melt quenching technique.
Appropriate amount of analytical grade reagent as strontium carbonate (SrCO$_3$), vanadium pentoxide (V$_2$O$_5$) and ferric oxide (Fe$_2$O$_3$) were used as starting materials. The compositions used during the synthesis are tabulated in the form of the table 5.1. According to stoichiometric proportion reagents were mixed together and ground for half an hour in order to have a homogeneous mixing. Then the mixture was poured into alumina crucible and kept in a muffle furnace 950 °C for 1h, until a bubble-free liquid was formed. The melt was quickly cooled at room temperature by pouring and pressing between two stainless steel plates. The as prepared palletized glass samples were powdered for further characterization.

5.3. Characterizations:

X-ray diffraction:

X-ray diffraction (XRD) patterns of the synthesized glass sample were recorded by using Philips (Model PW-3710) X-ray diffractometer. The XRD patterns recorded at room temperature.

Density and molar volume

The density “d” of the glasses was determined at room temperature using the Archimedes principle with acetone as an immersion liquid and also the molar volume calculated from the density data.

Fourier transforms infrared spectroscopy:

The Fourier transforms infrared (FTIR- BRUKER-TENSOR 37-FTIR-ATR instrument) spectra of all the samples in the wavelength range of 850–1500 cm$^{-1}$ were recorded at room temperature.

UV spectroscopy:

The optical absorption spectra of these glasses were recorded using UV-Perkin Elmer absorption spectrophotometer in the wavelength range 300 – 800 nm at normal incidence.
DC electrical conductivity:

The temperature dependence of DC electrical conductivity of all the glass samples was measured using the standard two-probe method in the temperature range of 300 K to 500 K. For good electrical ohmic contact the pellets were polished and silver paste was applied on both the surfaces of the pellets.

Dielectric properties:

The frequency dependence of dielectric properties was measured as a function of frequency in the range of 10 kHz-1MHz using a LCR-Q meter bridge (Model Hp 4248A) at room temperature.

5.4. Results and discussion

5.4.1. The X-ray diffraction (XRD)

The X-ray diffractions (XRD) of the prepared glass samples (10-x) SrO-xFe$_2$O$_3$-V$_2$O$_5$ are shown in Figure 5.1. The perusal of XRD patterns shows the presence of broad hump and absence of any sharp peaks. In XRD patterns, the presence of a broad diffuse scattering at low angles instead of crystalline peaks, confirms a long range structural disorder characterized of amorphous network.

Density and molar volume Density:

The densities of the prepared glasses were measured at room temperature using the Archimedes displacement method in which acetone was used as immersing liquid. The density was calculated according to the formula [45].

$$d_B = \frac{W_A}{W_A - W_B} \times d_{ace} \quad \ldots \ldots \ldots (5.1)$$

Where, $W_A$ = in weight of the sample in air, $W_B$ is weight of sample in acetone and $d_{ace}$ ($\rho = 0.791$ gm/cm$^3$) is the density of acetone. The values of bulk densities are given in table 5.2 and it may be observed that the density linearly increase from 3.10 to 3.20 cm$^3$ with the increase in Fe$_2$O$_3$ concentration in the glass.
composition as shown in Fig.5.2 (a).

**Molar volume:**

The corresponding molar volumes were calculated by using the relation, 
\[ V_m = \frac{M}{\rho}, \]
where M is the molecular weight and \( \rho \) is the density of corresponding glass samples. The molar volume values are shown in table 5.2. The molar volume gradually decreases from 57.55 to 56.01 cm\(^3\) with the increase of Fe\(_2\)O\(_3\) concentration as shown in Fig.5.2 (b).

**Hopping distance:**

The hopping distance (R) was determined by the equation given below and its value gradually decreases from 4.57 to 4.53 Å with increasing Fe\(_2\)O\(_3\) concentration (given in table 5.2) [46, 47].

\[ R = \left| \frac{M}{N_0 \rho_{\text{expt}}} \right|^{\frac{1}{2}} \] ......... (5.2)

Where, M is the molecular weight, \( N_0 \) is Avogadro’s number, \( \rho_{\text{expt}} \) is experimental density.

**Polaron radius:**

The Polaron radius (\( r_p \)) was calculated by the equation given below and its value decreases from 1.842 to 1.825 Å with increasing Fe\(_2\)O\(_3\) concentration.

\[ r_p = (\frac{1}{2})(\frac{\pi}{6})^{\frac{1}{3}} \cdot R \] ......... (5.3)

**Numbers of ions:**

Numbers of ions per cm\(^3\) which take part in the conduction process of the glass sample were calculated by using the relation below,

\[ N = \frac{\pi}{48r_p^3} \] ......... (5.4)

The number of ions value increases from 1.046 to 1.075 cm\(^3\)×10\(^{-22}\) with increasing
Fe₂O₃ concentration.

5.4.2. Fourier transforms infrared spectra (FTIR)

In Fig. 5.3 (a-e) is show the room-temperature IR spectra in the range of 850 to 1500 cm⁻¹ for different glass compositions and also for the crystalline V₂O₅ for comparison. In Fig. 5.3 (a-e), we see that for V₂O₅ a strong band exists at 1020 cm⁻¹, which has been assigned to the vibration of the isolated V₄O vandal groups in VO₅ trigonal bipyramid [48]. With the introduction of SrO and Fe₂O₃, changes of this group are observed in the spectra. Dimitriev and coworkers [49] have reported earlier that in glasses containing V₂O₅ and SrO the band exists at 1020 cm⁻¹. In this glass system containing V₂O₅, Fe₂O₃ and SrO exists along with the formation of new bands in the range 932 to 977 cm⁻¹. Glasses containing 90 mol% V₂O₅ show bands in the range 1065 to 1112 cm⁻¹ respectively. The addition on Fe₂O₃ new absorption bands are formed in Fig. 5.3(b-e) band in the range 1254, 1286 cm⁻¹ to 1290 cm⁻¹, 1320 cm⁻¹ have been assigned to symmetric and asymmetric stretching vibrations of the isolated VO₂ groups in VO₄ polyhedral [50-51].

Thus, from the present studies we observe that there is a pronounced effect of the introduction of SrO and Fe₂O₃ on the V₄O bonds that are present in the VO₅ polyhedral in crystalline V₂O₅. According to the structural model reported earlier, Sr ions may either occupy positions in the vanadate chain itself or may be located between vanadate chains and layers. In the first case, Sr ions will break up some of the V–O–V bonds and form new V–O–Sr bridges. The influence of Sr ions on the V₄O bonds in the glasses is restricted and it may have an indirect manifestation. This is the case for glasses containing 90 % V₂O₅, where a preservation of the band at 1020 cm⁻¹ in the IR spectra has been observed. On the other hand, in the second
case Fe ions interact directly with the V$_4$O bonds, as a result of which these bonds will be longer and the frequencies of the vibration should be shifted to higher wave numbers. The shift of the bands to higher wave numbers band in the range 1065 to 1112 cm$^{-1}$ for the glasses with 90 mol% V$_2$O$_5$, respectively, implies that Fe ions in these compositions are located between vanadate chains and layers. For these glasses, the glass structure consists of VO$_4$ polyhedral.

### 5.4.3. Ultraviolet-visible spectra (UV-VIS)

The optical absorption spectra are shown in Figs. 5.4(a-e). The absorption coefficient ($\alpha$), near the edge of each spectrum was calculated using the relation. The absorption coefficient ($\alpha$) was calculated at different photon energies by using the relation [52, 53].

$$\alpha = 2.303 \frac{A}{d} \quad \ldots \ldots \ldots \ (5.5)$$

Where, $A$ is the absorbance and $d$ is the thickness of the samples.

Optical transitions are basically two types, direct and indirect transitions. In these transitions, electromagnetic radiation interacts with the electrons in the valence band which reaches to conduction band by gaining fundamental band gap. These transitions occur in both crystalline and amorphous semiconductor materials. These transitions are related Mott's and Devi’s relation [54]. For photon energies just above fundamental edge, the relation between absorption coefficient ($\alpha$) and photon energy is given bellow.

$$\alpha = B \left( \frac{(h\nu-E_g)^n}{h\nu} \right) \quad \ldots \ldots \ldots \ (5.6)$$

Where, $B$ is a constant related to the extent of the band tailing, $h\nu$ is the photon energy, $E_g$ is the optical band gap energy and the exponent $n$ is a parameter which depends on the type of electronic transition responsible for absorption. The Tauc plots were plotted for various values of $n$, that is, 1/2 and 2, corresponding to direct
allowed and indirectly allowed. The plots the grapes variation of \((\alpha h\nu)^{1/2}\) vs. with \(h\nu\) (Tauc’s plot) is shown in Fig. 5.5(a-e). To estimate the values of \(E_g\), the linear region of the curves is extrapolated to meet the \(h\nu\) axis at \((\alpha h\nu)^{1/2} = 0\) and are listed in Tables 5.3. The values of refractive index for various compositions have been determined from the optical energy band gap using the relation proposed by Dimitrov and Sakka [55].

\[
\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_g}{2\nu}} \quad \cdots \cdots \cdots (5.7)
\]

The refractive indexes of the glass sample are in table 5.3. The variation of refractive index as a function \(\text{Fe}_2\text{O}_3\) composition \((x)\) as shown in Fig. 5.6(a). It is observed that the refractive indexes decreases gradually with the increase in \(\text{Fe}_2\text{O}_3\) content due to increase of bridging oxygen’s which influences the refractive index of glasses because the polarity of bridging oxygen’s is lower than that of non-bridging oxygen’s. The optical band gaps of glass sample are given in table 5.3. The variation of optical band gaps as a function \(\text{Fe}_2\text{O}_3\) composition \((x)\) as shown in Fig. 5.6(b). It is observed that the optical band gaps increases with the increase in \(\text{Fe}_2\text{O}_3\) content related to the progressive decrease in non-bridging oxygen atoms.

The dielectric constant \((\varepsilon)\) was calculated from the refractive index of the glass using given equation [56].

\[
\varepsilon = n^2 \quad \cdots \cdots \cdots (5.8)
\]

The dielectric constant of the glass samples are represent in table 5.3. It is observed that the optical dielectric constant of decreases with an increase in \(\text{Fe}_2\text{O}_3\) composition.

### 5.4.4. D.C. conductivity

D.C. conductivity as shown in Figure 5.7, the logarithmic conductivity in the temperature range \((300–500 \text{ K})\) exhibits a linear dependence on reciprocal
temperature. The temperature dependence of DC conductivity \( \sigma \) for the different glass compositions is shown in Fig.5.7, as a function of reciprocal temperature. It is observed that conductivity increases smoothly with increasing temperature, which is a characteristic of the hopping conduction in amorphous semiconductors. DC conductivity increases but the activation energy decreases with increase in \( \text{Fe}_2\text{O}_3 \) content. Conductivity in these electrons conductivity due to electron hopping from one valence state \( \text{Fe}^{2+} \) to the other valence state \( \text{Fe}^{3+} \)[57].

The mechanism of such transport of electrons is usually termed as “small polaron hopping” between Fe ions under different valence states, \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \). This is small polaron hopping (SPH) conduction mechanism in transition metal oxide glasses [58-60]. The composition dependence of DC conductivity indicates that the conductivity increases with the increasing \( \text{Fe}_2\text{O}_3 \) content. The activation energy calculated from the slope of the graphs (Figure 5.7) is listed in Table 5.4. It is clear from Figure 5.8 that the activation energy decreases with increasing \( \text{Fe}_2\text{O}_3 \) content. The composition dependence of DC conductivity at 400K and activation energy (Figure 5.8), indicates that the variation “W” with composition is much faster for the present glass system than those for the traditional vanadate glasses. It is observed that as the concentration of \( \text{Fe}_2\text{O}_3 \) increases, the activation of electrical conduction decreases and electrical conductivity increases. The value of the activation energy of electrical conductivity is similar to those of \( \text{V}_2\text{O}_5\)-BaO-B\(_2\)O\(_3\) glasses and \( \text{Fe}_2\text{O}_3\)-B\(_2\)O\(_3\)-V\(_2\)O\(_5\) [61, 62]. The change in conductivity and activation energy may help to detect the structural changes as a consequence of increasing of \( \text{Fe}_2\text{O}_3 \) content and decreasing of strontium oxide content. Generally, it is known that the addition of \( \text{Fe}_2\text{O}_3 \) in \( \text{V}_2\text{O}_5 \) glasses increases the conductivity as a result of increasing of nonbridging oxygen ions [63]. According to this theory, the
conduction process at higher temperature is considered in terms of optical phonon assisted hopping of small polaron between localized states. The dc conductivity in adiabatic region is given a table (5.4)

\[ \sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right) \]  \hspace{0.5cm} (5.9)

Where, \(\sigma_0\) is a pre-exponential factor, \(W\) is the activation energy, \(k\) is the Boltzmann constant, and \(T\) is temperature in Kelvin.

In Mott's model [64-66] for conduction process in the transition metal oxide glasses, the conduction mechanism is considered in terms of the optical phonon assisted hopping of small polaron between localized states. According to this model, the DC conductivity for the nearest-neighbor hopping in non-adiabatic regime at high temperatures \((T>\theta_D/2)\) is given by.

\[ \sigma = \frac{v_0 ne^2 R^2}{kT} C(1-C) \exp(-2\alpha R) \exp\left(-\frac{W}{kT}\right) \]  \hspace{0.5cm} (5.10)

where, \(C\) is the fraction of reduced valence sites of the transition metal ions, \(v_0\) is the longitudinal optical phonon frequency, \(N\) is the number of metal ion sites per unit volume, \(R\) is the hopping distance and, \(W\) is the activation energy for hopping conduction, \(\alpha\) is the tunneling factor (the ratio of wave function decay). Assuming that a strong electron lattice interaction exists, the activation energy \(W\) is the result of polaron formation with bonding energy \(W_p\) and any energy difference \(W_D\) which might exist between the initial and final sites due to variation of the local arrangements of ions. Austin and Mott have shown that

\[ W = W_H + (1/2)W_D \text{ for } T > \theta_D / 2, \]  \hspace{0.5cm} (5.11)

\[ W = W_D \text{ for } T > \theta_D / 4, \]  \hspace{0.5cm} (5.12)

Where, \(W_H\) is the polaron hopping energy, and an energy difference \(W_D\) is the
Energy difference between two adjacent sites i.e. disorder energy and $\theta_D$ is the Debye temperature. The polaron hopping energy is given a table (5.4)

$$W_H = \frac{e^2}{4\varepsilon_p} \left( \frac{1}{r_p} - \frac{1}{R} \right) \quad \text{................ (5.13)}$$

Where,

$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon^\infty} - \frac{1}{\varepsilon^S} \quad \text{......... (5.14).}$$

$\varepsilon^\infty$ and $\varepsilon^S$ the static and high frequencies dielectric constants of the glasses. An estimate of $W_H$, can be made from eq. (5.13) the values of $W_H$ are represent table 5.4 and $\varepsilon_p$ is an effective optical dielectric constant are given a table (5.3).

Where, $W_p$ is the polaron binding energy is given by table 5.4

$$W_H = W_p / 2 \quad \text{.......... (5.15)}$$

The density of states $N (E_F)$, for thermally activated electron hopping near the Fermi level is calculated by the following relation [67].

$$N(E_F) = \frac{3}{4\pi WR^3} \quad \text{......... (5.16)}$$

And the calculated values are of the order of $10^{21}$ eV$^{-1}$ cm$^{-3}$ (Table 5.4) which is localized states [68-70]. The density of states $N (E_F)$ at the Fermi level decreases with increasing Fe$_2$O$_3$ content.

### 5.4.5. Dielectric

Dielectric constant ($\varepsilon'$) represent the polarizability of the material. For transition metal oxide glasses, its dielectric properties are mainly due to ionic motions. It is well known that charge carriers in glass cannot move freely through a glass matrix but they can be displaced and polarized as a response to an applied
alternating field [71]. Owen [72]. Pointed out that the dipoles of relatively immobile ions which also take part in network-coming may also contribute to the electrical properties. The significance of the complete dipolar response can be interpreted in the region near the loss peak frequency, up which his dominated by the dipolar transitions [73]. Transition metal oxide glasses, the dielectric properties mainly arise from the ionic motions. The free energy barriers impeding the ionic diffusion, however, can be expected to vary from site to site, so there are different ionic motions in glasses. The first is the rotation of ions around their negative site and the second is short distance transport, i.e. ions hop out of sites with low free energy barriers and tend to pile up at sites with high free-energy barriers in the electric field direction in D.C. or low frequency electric field or oscillate between the sites with high free-energy barriers in an A.C. electric field. Both the first and the second motions make a contribution to the dielectric constant (\(\varepsilon'\)) of glasses [74].

The variation of dielectric constant (\(\varepsilon'\)) as a function of frequency is shown in Fig. 5. It is observed from these figures that the dielectric constant decreases continuously with increase in frequency for all the samples followed by a frequency independent behavior. The entire prepared glass sample has exhibited the same trend of rapid decrease in dielectric constant with an increase in the frequency and finally reaching to a constant value. The behavior of dielectric constant is similar to the behavior of other oxide glasses [75, 76]. At low frequencies, dielectric constant profile exhibits a high dispersion, because the ions are not in a position to diffuse them along with the electric field direction and as a
result, charges accumulate in the space charge region at the electrode electrolyte interface due to net polarization effect. At higher frequencies, the periodic reversal of the electric field at interface occurs so fast that no excess ions accumulate in the electric field direction [77] and hence, the dielectric constant is lowered by weakening of ion-ion interaction in the dipoles and as a result their contribution to the polarization would be reduced.

The dielectric loss factor ($\varepsilon''$) was determined using equation (3.6). The dielectric loss ($\varepsilon''$) as function is an important part of the total core loss in oxide glasses. The dielectric loss factor as a function of frequency for all the compositions is shown in Fig. 5.10. The dielectric loss behavior is similar to that of dielectric constant. It may be due to the increase in hopping electrons resulting in a local displacement in the direction of the extent dielectric loss.

The dielectric loss tangent (tan $\delta$) represents the energy dissipation in the dielectric system. The dielectric loss tangent was determined using the relation (3.5). Fig.5.11. shows the variation of tan $\delta$ with frequency at room temperature for transition metal ion for oxide glasses. It is observed that dielectric loss tangent of the prepared glass system decreases with an increase in frequency Dielectric loss tangent has a high dispersion at low frequency is attributed to interfacial polarization mechanism, which decrease gradually with a tailing edge as frequency increases due to low reactance offered by the glasses causing less contribution of ions in the direction of the applied field, could also be due to domination of the polarization by migrating charges in the lower frequency and lower dipole relaxations in the higher frequency. The absence of relaxation peaks in the
dielectric loss spectra also indicates the short range ionic conduction due to hoping of charges in the dielectric response at lower frequency [78-80].

5.5. Conclusions

The oxide glass samples having a composition (10-x) SrO - x.\(\text{Fe}_2\text{O}_3\)- 90 \(\text{V}_2\text{O}_5\), where, \(x = 0, 02, 04, 06\) and 08 mole % were successfully prepared by melt quenching technique. The XRD analysis did not show any sharp peaks and confirms that the glass samples are amorphous in nature. It has been found that, \(\text{Fe}_2\text{O}_3\) played an important role in the glass network, by increasing the concentration of \(\text{Fe}_2\text{O}_3\) density increases and molar volume decreases. The hopping distance and polaron radius decrease with \(\text{Fe}_2\text{O}_3\) concentration.

The FTIR spectra of the prepared glass samples indicated the formation of glass functional groups. The band gap energy increases with increase in iron concentration, and refractive index decreases with the increase in the \(\text{Fe}_2\text{O}_3\) content. Absorbance, absorbance coefficient decreases and optical dielectric constant decreases with the increase in the \(\text{Fe}_2\text{O}_3\) content.

The DC conductivity of the ternary glass system has been studied over a temperature range 300 to 500 K. The conductivity has been found to depend on the concentrations of \(\text{Fe}_2\text{O}_3\) and the temperature DC conductivity was found to increase where as activation energy was found to decrease with the increases in the \(\text{Fe}_2\text{O}_3\) content. As \(\text{Fe}_2\text{O}_3\) concentration increases, polarons binding energy and polaron hoping energy increases. The density of state at Fermi level increases with \(\text{Fe}_2\text{O}_3\) concentration.The conduction in the present glass system was confirmed to be a result of primarily adiabatic hopping of small polaron between TMIs. The dielectric properties (\(\varepsilon'\) and \(\tan \delta\)) of these glasses are found to be decreases with
an increase in frequency due to accumulation of charges at the electrode-electrolyte interface hence results in with polarization effect.
References


Table 5.1: Coding for the samples and composition (mol %)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition (mol %)</th>
<th>SrO</th>
<th>Fe₂O₃</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFV1</td>
<td></td>
<td>10</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>SFV2</td>
<td></td>
<td>08</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>SFV3</td>
<td></td>
<td>06</td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>SFV4</td>
<td></td>
<td>04</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>SFV5</td>
<td></td>
<td>02</td>
<td>8</td>
<td>90</td>
</tr>
</tbody>
</table>

SFV: Strontium oxide, Ferric-oxide, Vanadium pentoxide.

Table 5.2: Physical parameter: density (d), molecular weight (M), molar volume (Vₘ), number of ions cm³ (N), hopping distance (R) and polaron radius (rₚ)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>d (g/cm³)</th>
<th>M (g/mol)</th>
<th>Vₘ (cm³/mol)</th>
<th>N x10²²</th>
<th>R (Å)</th>
<th>rₚ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFV1</td>
<td>3.100</td>
<td>178.455</td>
<td>57.55</td>
<td>1.046</td>
<td>4.571</td>
<td>1.842</td>
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<td>3.122</td>
<td>178.696</td>
<td>57.23</td>
<td>1.052</td>
<td>4.563</td>
<td>1.838</td>
</tr>
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<td>3.154</td>
<td>178.937</td>
<td>56.72</td>
<td>1.061</td>
<td>4.549</td>
<td>1.833</td>
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<td>179.178</td>
<td>56.45</td>
<td>1.066</td>
<td>4.542</td>
<td>1.830</td>
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<td>SFV5</td>
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<td>179.419</td>
<td>56.01</td>
<td>1.075</td>
<td>4.530</td>
<td>1.825</td>
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</table>
Table 5.3: Optical parameters: wavelength ($\lambda'$), absorbance (A), coefficient of absorption ($\alpha'$), optical dielectric constant ($\varepsilon$), refractive index (n) and optical energy band gap ($E_{opt}$)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\lambda'$ (nm)</th>
<th>A</th>
<th>$\alpha'$ (cm$^{-1}$)</th>
<th>$\varepsilon$</th>
<th>n</th>
<th>$E_{opt}$ (eV)</th>
</tr>
</thead>
<tbody>
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<td>3.85</td>
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<td>5.421</td>
<td>2.33</td>
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<td>590</td>
<td>3.72</td>
<td>744</td>
<td>5.172</td>
<td>2.27</td>
<td>2.10</td>
</tr>
<tr>
<td>SFV4</td>
<td>563</td>
<td>3.63</td>
<td>726</td>
<td>5.042</td>
<td>2.24</td>
<td>2.20</td>
</tr>
<tr>
<td>SFV5</td>
<td>555</td>
<td>3.55</td>
<td>710</td>
<td>5.006</td>
<td>2.23</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Table 5.4: Polaron binding energy ($W_p$), polaron hopping energy ($W_h$), activation energy ($W$), D.C. conductivity ($\log \sigma$) at 400 K, density of state at Fermi level [$N(E_F)$]

<table>
<thead>
<tr>
<th>Sample code</th>
<th>W (eV)</th>
<th>$W_p$ (eV)</th>
<th>$W_h$ (ev)</th>
<th>$\log \sigma$ (Ohm$^{-1}$cm$^{-1}$)</th>
<th>$[N(E_F)]$ (ev$^{-1}$cm$^{-1}$)$\times10^{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFV1</td>
<td>0.32</td>
<td>0.428</td>
<td>0.214</td>
<td>-3.4061</td>
<td>3.13</td>
</tr>
<tr>
<td>SFV2</td>
<td>0.31</td>
<td>0.449</td>
<td>0.224</td>
<td>-3.1790</td>
<td>3.15</td>
</tr>
<tr>
<td>SFV3</td>
<td>0.29</td>
<td>0.472</td>
<td>0.236</td>
<td>-3.0492</td>
<td>3.18</td>
</tr>
<tr>
<td>SFV4</td>
<td>0.28</td>
<td>0.485</td>
<td>0.242</td>
<td>-2.9168</td>
<td>3.20</td>
</tr>
<tr>
<td>SFV5</td>
<td>0.26</td>
<td>0.490</td>
<td>0.245</td>
<td>-2.6914</td>
<td>3.22</td>
</tr>
</tbody>
</table>
**Figure 5.1.** XRD pattern for (10-x) SrO - xFe₂O₃- 90 V₂O₅, (for x = 0, 2, 4, 6 and 8 mole %) glass system
Figure 5.2(a). Variation of density ($d$) with Fe$_2$O$_3$ content.

Figure 5.2(b). Variation of molar volume ($V_m$) with Fe$_2$O$_3$ content.
Figure 5.3(a). Room temperature IR spectra of (10SrO-90 V2O5) glass.

Figure 5.3(b). Room temperature IR spectra of (8SrO-2Fe2O3-90 V2O5) glass.
Figure 5.3(c). Room temperature IR spectra of (6SrO-4Fe₂O₃-90 V₂O₅) glass.

Figure 5.3(d). Room temperature IR spectra of (4SrO-6Fe₂O₃-90 V₂O₅) glass.
Figure 5.3(e). Room temperature IR spectra of (2SrO-8Fe$_2$O$_3$-90 V$_2$O$_5$) glass.

Figure 5.4(a). Optical absorption as a function of wavelength for the glass system (10SrO-90V$_2$O$_5$).
**Figure 5.4(b).** Optical absorption as a function of wavelength for the glass system

$(8\text{SrO}-2\text{Fe}_2\text{O}_3-90\text{V}_2\text{O}_5)$

**Figure 5.4(c).** Optical absorption as a function of wavelength for the glass system

$(6\text{SrO}-4\text{Fe}_2\text{O}_3-90\text{V}_2\text{O}_5)$. 
Figure 5.4(d). Optical absorption as a function of wavelength for the glass system 

\[(4\text{SrO}-6\text{Fe}_2\text{O}_3-90\text{V}_2\text{O}_5)\]

Figure 5.4(e). Optical absorption as a function of wavelength for the glass system 

\[(2\text{SrO}-8\text{Fe}_2\text{O}_3-90\text{V}_2\text{O}_5).\]
Figure 5.5(a). Tauc’s plots for (10SrO-90V2O5) glass ($r = 1/2$).

Figure 5.5(b). Tauc’s plots for (8SrO-2Fe2O3-90V2O5) glass ($r = 1/2$).
Figure 5.5(c). Tauc’s plots for (6SrO-4Fe₂O₃-90V₂O₅) glass (r =1/2).

Figure 5.5(d). Tauc’s plots for (4SrO-6Fe₂O₃-90V₂O₅) glass (r =1/2).
Figure 5.5(e). Tauc’s plots for (2SrO-8Fe₂O₃-90V₂O₅) glass \((r=1/2)\).

Figure 5.6(a). Variation of refractive index \((n)\) with \(\text{Fe}_2\text{O}_3\) Content.
Figure 5.6(b). Variation of optical energy band gap $E_{\text{opt}}$ with Fe$_2$O$_3$ content.

Figure 5.7. Temperature dependence of dc conductivity as a function of reciprocal temperature for (10-\(x\))SrO-\(x\)Fe$_2$O$_3$-90V$_2$O$_5$ glasses.
**Figure 5.8.** Variation of Activation energy (W) with Fe$_2$O$_3$ content.

**Figure 5.9.** Variation of dielectric constant ($\varepsilon'$) with frequency at room temperature of (10-$x$)SrO-$x$Fe$_2$O$_3$-90V$_2$O$_5$ ($0 \leq x \leq 08$).
Figure 5.10. Variation of dielectric loss ($\varepsilon''$) with frequency at room temperature of (10-$x$)SrO-$x$Fe$_2$O$_3$-90V$_2$O$_5$ ($00 \leq x \leq 08$).

Figure 5.11. Variation of dielectric loss tangent (tan $\delta$) with frequency at room temperature of (10-$x$)SrO-$x$Fe$_2$O$_3$-90V$_2$O$_5$ ($00 \leq x \leq 08$).