CHAPTER IV

AC CONDUCTIVITY AND ELECTRIC MODULUS STUDIES OF SCV, SCP, SCA AND SBS SAMPLES

4.1. A.C. THEORY
4.1.1. Impedance Spectroscopy
4.1.2. Dielectric Permittivity
4.1.3. Electric Modulus
4.1.4. Jonscher's Power Law

4.2. RESULTS AND DISCUSSION
4.2.1. Complex Impedance
4.2.2. Frequency Dependence of Conductivity
4.2.3. Dielectric Permittivity
4.2.4. Electric Modulus

4.3. CONCLUSIONS

REFERENCES
CHAPTER IV

A.C. CONDUCTIVITY AND ELECTRIC MODULUS STUDIES OF
SCV, SCP, SCA AND SBS SAMPLES

One of the important techniques to characterize many of the electrical and electrochemical properties of fast ionic conductors is the conductivity spectroscopy [1-3]. In general, conductivity measurements are made by applying the d.c. bias across the material, but it results in the polarization at the electrode-electrolyte interface, which opposes the applied field and hence, the ionic current falls with time. To overcome this problem, the four-probe or two reversible electrode methods are adopted to measure d.c. conductivity of the materials [2]. Later, the single frequency measurements are carried out, but these methods are found to be inadequate for understanding the complete electrical behavior of the materials, since the electrochemical processes represented by various individual elements (R, C & L) are frequency dependent [6, 7]. Hence, the a.c. technique has been developed to measure impedance over a range of frequencies to estimate the exact bulk conductivity and frequency dependent conductivity in FICs. From the impedance study, one can obtain not only the bulk conductivity but also grain boundary effects, ionic transport, double layer formation at the electrode/electrolyte interface, etc. Hence, in recent years, Impedance Spectroscopy (IS) has become a powerful technique for characterizing the electrical properties of the FIC materials and their interfaces with electronically conducting electrodes. Also, the IS measurements can provide the dynamic properties to understand the microscopic nature of the FIC materials [2, 5, 6].

Impedance Spectroscopy is also called Impittance Spectroscopy (IS) and it is used to measure complex impedance $Z^*$, complex admittance $Y^*$, complex dielectric permittivity $\varepsilon^*$ and complex modulus $M^*$ [2,9]. This chapter briefly
describes the a.c. theory, measurement & analysis of impedance data, a.c. conductivity and electric modulus. It also gives the detailed discussion of temperature dependent of conductivity, ac conductivity, dielectric permittivity and electric modulus studies to understand ion dynamics in the glassy systems.

4.1. A.C. THEORY

4.1.1. Impedance Spectroscopy

The complex impedance $Z(\omega)$ is defined as ratio of voltage $V(t)$ to current $I(t)$ in the time domain on applying a sinusoidal signal of low amplitude across a solid electrolyte

\[ V(t) = V_0 \exp(j\omega t) \]  
\[ I(t) = I_0 \exp(j\omega t - \phi) \]

\[ Z(\omega) = |Z| \exp(-j\phi) \]  
\[ Z(\omega) = |Z| \cos\phi - j |Z| \sin\phi \]

where $|Z|$ is magnitude and $(\phi)$ is phase angle.

Impedance or Immittance spectroscopy means any one of the following four quantities

Complex impedance \[ Z^* = Z' - jZ'' \]

Complex Admittance \[ Y^* = Y' + jY'' = 1/Z^* \]

Complex permittivity \[ \varepsilon^* = \varepsilon' - j\varepsilon'' = 1/j\omega C_0 Z^* \]

Complex modulus \[ M^* = M' + jM'' = j\omega C_0 Z^* \]

where $j = \sqrt{-1}$, $C_0$ is the vacuum capacitance and $\omega = 2\pi f$ is the angular frequency.
The admittance and permittivity are parallel functions characteristic at low frequencies whereas the impedance and modulus are series functions at high frequencies [1, 6].

The complex plane is used to represent the electrical quantities of real and imaginary parts of complex impedance ($Z^*$), complex admittance ($Y^*$), complex permittivity ($\varepsilon^*$) and complex modulus ($M^*$) [5, 7]. The impedance and admittance representations for the parallel & series combinations of an ideal RC circuit elements are discussed.

In series: The complex impedance for the series combination of resistance $R_s$ and capacitance $C_s$ is given by

$$Z^* = Z - j\frac{1}{\omega C_s}$$

$$Z^* = Z' - jZ''$$

where $Z' = R_s$ and

$$Z'' = \frac{1}{\omega C_s}$$

Fig. 4.1.a shows the resultant impedance for $R$ & $C$ in series is represented by a vertical line parallel to the imaginary axis intersecting the real axis at $R$. The corresponding admittance plot gives the semicircle intersecting the real axis at the origin and at a point $1/R$ as shown in fig. 4.1. b.

In parallel: The complex impedance for the parallel combination of $R_p$ and $C_p$ is given by

$$\frac{1}{Z^*} = \frac{1}{R_p} + j\omega C_p$$

$$Z^* = Z' - jZ''$$

where,
Fig. 4.1. a) $Z''$ vs. $Z'$ & b) $B$ vs. $G$ for series and c) $Z''$ vs. $Z'$ & d) $B$ vs. $G$ for parallel combinations of RC circuits
The complex impedance for a parallel combination of $R_p$ & $C_p$ represents a semicircle, as shown in the Fig.4.1. c, intersecting the real axis at origin & at a point $R$. The difference between the two intercepts gives the bulk resistance ($R_b$) of the material. The equation of a circle with radius $R/2$ and center at $(R/2,0)$ is obtained from equations 4.10 & 4.11.

$$Z' = \frac{R_p}{[1 + (\omega R_p C_p)^2]} \quad 4.10$$

$$Z'' = \frac{\omega R_p^2 C_p}{[1 + (\omega R_p C_p)^2]} \quad 4.11$$

$$\left(Z' - \frac{R}{2}\right)^2 + Z''^2 = \frac{R^2}{4} \quad 4.12$$

The corresponding complex admittance plot shown in fig. 4.1.d gives the straight line parallel to the imaginary axis intersecting the real axis at $1/R$. The relationship between the parallel and series components is obtained from the equations 4.7, 4.8, 4.10 & 4.11.

$$R_s = \frac{R_p}{[1 + (\omega R_p C_p)^2]} \quad 4.13$$

$$C_s = \frac{[1 + (\omega R_p C_p)^2]}{\omega^2 R_p^2 C_p} \quad 4.14$$

Fig.4.2. a & b show the equivalent circuits & the impedance plots respectively for an ideal and real solid electrolytes. From the fig. 4.2.a, it is observed a vertical straight line and a perfect semicircle in the impedance plot for an ideal solid electrolyte. From the fig. 4.2.b, it is observed that the inclined straight line is due to the presence of double layer capacitance of electrode-electrolyte interface and the depressed semicircle corresponds to the parallel combination of resistance and capacitance. The angle of inclination of the straight line and angle of depression of the semicircle are due to the distributed
Fig. 4.2. Impedance spectra of a) ideal, b) real & c) polycrystalline solid electrolytes.
microscopic material properties, termed as constant phase element (CPE) [8,9].

The complex impedance of the real solid electrolyte is represented as

\[ Z^* = K(j\omega)^\alpha \]  

where \( 0 \leq \alpha \leq 1 \). When \( \alpha = 0 \), \( Z \) is frequency independent and \( K \) is the resistance \( R \), where as, when \( \alpha = 1 \), \( Z = -jK/\omega \), the CPE corresponds to capacitance \( C \). The fractional power law dependence on frequency is referred to as a constant-phase-angle element or non-Debye capacitor [10, 11]. From the fig 4.2.b, the equivalent circuit for real solid electrolyte is given by the parallel combination of CPE and bulk resistance in series with CPE of the interface.

Fig 4.2.c shows the impedance spectrum for a polycrystalline sample with the two semicircles, one due to resistance within the grains of the materials and other due to the partial or complete blocking of charge carriers at grain boundaries. From the fig. 4.2 c, the equivalent circuit for the polycrystalline samples is given by the series of parallel combination of CPE & bulk resistance, CPE & grain boundary resistance and the CPE of the interface. The grain boundaries may act as a hindrance to the ionic transport or may also contribute to the high conduction path due to the presence of large defect density in the interfacial region [7, 8, 12, 13].

The complex impedance analysis has been performed using A.Boukamp's equivalent circuit software, in which non-linear least square (NLLS) fitting procedure is adopted [14]. The NLLS fitting is performed in two steps, i) by the partial NLLS fit, where the suitable points are selected on the straight line part of the impedance data through which a tangential line is drawn. The intersection of the line with the real axis gives the bulk resistance. ii) by choosing a set of three data points in the high frequency depressed semicircle, a semicircle is fitted through origin and the partial NLLS fit gives the
values for the resistance and CPE parameters. The entire impedance distribution is simultaneously fitted to the NLLS fit to obtain a set of parameters (e.g. circuit elements) for the equivalent circuit. The most of systematic errors are reduced and the parameters of the complex equivalent circuit are obtained.

### 4.1.2. Dielectric Permittivity

If a varying field $V(t)$ is applied to a material, then the polarization and induced charge $Q$ are related as [15]

$$ Q = \varepsilon^* V_0 \exp(j\omega t) $$

where $\varepsilon^*$ is the complex dielectric constant. The frequency dependent complex dielectric permittivity is given by

$$ \frac{(\varepsilon^* - \varepsilon_o)}{(\varepsilon_s - \varepsilon_o)} = \frac{1}{1 + j\omega \tau} $$

where $\varepsilon_s$ and $\varepsilon_o$ are the low and high frequency dielectric constants respectively, $\omega = 2\pi f$ is the angular frequency, $\tau$ is the time constant. The $\varepsilon^*$ is given by

$$ \varepsilon^* = \varepsilon' - i\varepsilon'' $$

where $\varepsilon'$ is the relative permittivity or dielectric constant, $\varepsilon''$ is the dielectric loss. Separating the real and imaginary parts of the equation 4.17,

$$ \varepsilon' = \varepsilon_s + \frac{(\varepsilon_s - \varepsilon_o)}{(1 + \omega^2 \tau^2)} $$

$$ \varepsilon'' = \frac{(\varepsilon_s - \varepsilon_o) \omega \tau}{(1 + \omega^2 \tau^2)} $$

$$ \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_o) \omega \tau}{\varepsilon_s + \varepsilon_o \omega^2 \tau^2} $$
Fig. 4.3. Dielectric parameters a) $\varepsilon'$, b) $\varepsilon''$ & c) $\tan \delta$ as function of frequency.
The above eqns. 4.19 to 4.21 are called Debye equations and fig. 4.3.a, b & c show respectively $\varepsilon'$, $\varepsilon''$ & $\tan \delta$ as a function of frequency for an ideal material [15]. In fig. 4.3 a, $\varepsilon'$ is independent of frequency at low frequencies and with increasing frequency, it passes an inflection at $\omega = 1/\tau$ and also, at higher frequencies, it becomes asymptotic to $\varepsilon_\infty$. In the fig. 4.3 b, the $\varepsilon''$ exhibits a maximum at $\omega \tau = 1$, where the oscillating charges are coupled with the oscillating field & absorbs a maximum electrical energy. From the fig. 4.3.c, it is found that $\tan \delta$ exhibits a symmetric Debye behavior with a loss tangent maximum at $\omega \tau = (\varepsilon_\infty / \varepsilon_\infty)^{1/2}$.

Many real materials show a deviation from an ideal equations and exhibit a non-Debye dielectric behavior. The non-Debye dielectric response can be described using Cole-Cole, Davidson-Cole and empirical expression proposed by Havriliak-Negami (H-N) [16 - 18].

The dielectric permittivity $\varepsilon^*$ is related to complex impedance $Z^*$ by

$$\varepsilon^* = \frac{1}{j\omega C_o Z^*}$$  \hspace{1cm} (4.22)

$\omega$ is the angular frequency and $C_o = t/A\varepsilon_o$ is the capacitance of free space.

$$\varepsilon' = \frac{t}{\omega A\varepsilon_o} \left[ \frac{Z''}{Z'^2 + Z''^2} \right]$$  \hspace{1cm} (4.23)

$$\varepsilon'' = \frac{t}{\omega A\varepsilon_o} \left[ \frac{Z'}{Z'^2 + Z''^2} \right]$$  \hspace{1cm} (4.24)

In the present study, the real and imaginary parts of the dielectric permittivity are calculated using the above equations 4.23 & 4.24, pellet dimensions and the measured impedance data.
4.1.3. Electric Modulus

The complex electric modulus is defined by the reciprocal of the complex permittivity [1].

\[ M^* = \frac{1}{\varepsilon^*} = j\omega \varepsilon' Z^* \]  \hspace{1cm} 4.25

\[ M^* = M' + jM'' = j\omega \varepsilon' (Z' + jZ'') \]  \hspace{1cm} 4.26

where \( M^* \) is the complex modulus, \( \varepsilon^* \) is the dielectric permittivity, \( M' \) is the real and \( M'' \) is the imaginary parts of modulus.

The complex electric modulus spectrum represents the measure of the distribution of ion energies or configurations in the structure and it also describes the electrical relaxation and microscopic properties of ionic glasses [19, 20]. The modulus formalism has been adopted as it suppresses the polarization effects at the electrode/electrolyte interface. Hence, the complex electric modulus \( M(\omega) \) spectra reflects the dynamic properties of the sample alone.

For parallel combination of RC element, the real and imaginary parts of the modulus are given by

\[ M' = \frac{R^2 C \omega}{[1 + (\omega CR)^2]} \frac{\varepsilon_0 \varepsilon'' Z''}{t} \]  \hspace{1cm} 4.27

\[ M'' = \frac{R C \omega}{[1 + (\omega CR)^2]} \frac{\varepsilon_0 \varepsilon'' Z''}{t} \]  \hspace{1cm} 4.28

Fig. 4.4.a shows the real \( M' \) vs. imaginary \( M'' \) parts of complex modulus spectrum for the parallel combination of RC by a semicircle intersecting the real
axis at 0 and $\varepsilon_0/C$. In the fig. 4.4.b, for an ideal solid electrolyte, the modulus $M''$ vs. $\log f$ represents the Debye curve with a single relaxation time and a maximum at $\omega\tau = 1$. In fig. 4.4.c, the impedance $Z''$ vs. $\log f$ give the Debye peak, the FWHM is found to be 1.44 decade and the corresponding $\beta$ value is 1, whose peak maxima coincide the peak of $M''$ vs. $\log f$ plot.

In case of real solid electrolyte, the modulus spectra exhibit a broad and asymmetric non-Debye nature with distribution of relaxation times. The variation of relaxation time is continuous and is represented by normalized function for the distribution of relaxation times $g(\tau)$ [21]. Then the relaxation function $\psi(t)$ in time domain is given by

$$\psi(t) = \int_0^\tau d\tau g(\tau) \exp(-t/\tau) \quad 4.29$$

if the relaxation time $\tau$ is thermally activated, then

$$\tau = \tau_0 \exp(E_a / kT) \quad 4.30$$

where $E_a$ is the relaxation activation energy, $k$ is the Boltzmann constant, $T$ is the absolute temperature. In the frequency domain, the relaxation function is expressed in electric modulus as

$$M^* = M_0 \int_0^\tau d\tau g(\tau) [i\omega\tau / (1 + i\omega\tau)] \quad 4.31$$

$$M^* = M_0 (1 - N^*) \quad 4.32$$

$$N^* = \int dt \exp(-i\omega t) [-d\phi(t)/dt] \quad 4.33$$

88
Fig. 4.4. a) $M''$ vs. $M'$, b) $M''$ vs. $\log f$ and c) $Z''$ vs. $\log f$ plots of ideal RC elements.
where $\phi(t)$ is the decay function given by

$$
\phi(t) = \exp[-(t / \tau)\beta]
$$

$\beta$ is the stretched exponent, $\tau$ is the relaxation time. The $\phi(t)$ is the stretched exponential KWW relaxation function and is written as sum of exponential terms

$$
\phi(t) = \sum_{i=1}^{n} g_i \exp(-t / \tau_i)
$$

The $g_i$ coefficients are evaluated by linear least square fit of the above equations 4.35 & 4.36. The input parameters $\beta$, $M_s$ & $\tau$ for the fit are obtained from the measured modulus data and were fitted to the KWW function following the method described by Moynihan et al [21].

4.1.4. Jonscher's Power Law

A typical frequency dependence conductivity spectrum that shown in the fig. 4.5 exhibit three distinguish regime a) low frequency dispersed b) an intermediate plateau and c) conductivity dispersion at high frequency [15, 22 - 24]. The variation of conductivity in the low frequency region may be attributed to the polarization effects at the electrode-electrolyte interface. At very low frequencies, more charge accumulation occurs and hence, drop in conductivity. In the intermediate frequency region, conductivity is almost found to be frequency independent & equal to dc conductivity and at the high frequency region, the conductivity increases with frequency. The frequency dependence of electrical conductivity of solid electrolytes is explained by a simple expression given by Jonscher's power law. The power law relates the frequency dependent conductivity or the so-called universal dynamic response (UDR) of ionic conductivity and frequency by [25, 26]
Fig. 4.5. Schematic representation of log conductivity vs. frequency
\[ \sigma_a = \sigma_0 + A \omega^s \]

where \( \sigma_a \) is the ac conductivity, \( \sigma_0 \) is the limiting zero frequency conductivity \( (\sigma_{dc}) \), \( A \) is a pre-exponential constant, \( \omega = 2\pi f \) is the angular frequency and \( s \) is the power law exponent where \( 0 < s < 1 \).

4.2. RESULTS AND DISCUSSION

4.2.1. Complex Impedance

The real and imaginary parts of complex impedance measurements were made as a function of frequency as well as at low temperatures (120 to 300K) on the pressed pellets of type conducting electrode (silver) / sample / conducting electrode (silver) for formers, modifier to formers and dopant compositions of SCV, SCP & SCA glassy samples. The measured impedance data are analyzed using the equivalent circuit software developed by A.Boukamp. All the circuit parameters are adjusted simultaneously, in order to fit the measured data through NLLS procedure to obtain the bulk resistance and the equivalent circuit of the materials.

Fig. 4.6 a, b & c show the real \( (Z') \) and imaginary \( (Z'') \) parts of the impedance spectra obtained at various low temperatures (120 to 300K) for the high conducting dopant salt composition of SCV, SCP & SCA samples respectively. From the fig. 4.6 a, b & c, it is observed that with increase in temperature in the lower range 120K to 200K, the formation of complete depressed semicircle occurs and on further increase above 200K, the depressed semicircle starts disappear with a formation of an inclined straight line. From the above figures, it is observed that the intersection of the semicircle with the
real axis shifts towards the origin with increase in temperature and the frequency of the intersection with real axis also increase with temperature. Similar behavior is observed for the low temperature dependence of the impedance for former, modifier to formers and dopant composition respectively of SCV, SCP & SCA glassy samples. The analysis of the spectra by the NLLS fit yielded the values of the bulk resistance $R_b$ from the intercept of the semicircle with real axis. The electrical behavior of the samples is represented as the parallel combination of bulk resistance and distributed elements CPE due to the depressed semicircle.

The bulk conductivity is calculated using the bulk resistance obtained from the analyzed impedance data at the various temperatures (120K to 300K) and pellet dimensions for all the former, modifier to former and dopant salt compositions of SCV, SCP & SCA glassy samples. Fig. 4.7 a, b & c show the log ($\sigma$T) vs. 1000/T plots for all the dopant compositions of SCV, SCP & SCA glassy samples respectively. The temperature dependence of conductivity obeyed the Arrhenius relation & activation energy ($E_a$) is obtained from the slopes of the linear fit. Fig. 4.8 a, b & c show respectively the variation of $E_a$ with dopant salt composition of all the SCV, SCP & SCA systems.

From the fig. 4.6 a, b & c, it is observed that the depressed semicircle in high frequency region represents parallel combination of the bulk resistance and bulk capacitance of the glassy materials [27 - 29]. The center of the depressed semicircle displaced below the real axis and it may be due to the presence of distribution of various elements at the electrolyte-electrode system, which indicates that the relaxation time $\tau$ is not a single valued but distributed continuously around a mean value [1, 13]. Hence, the distribution of various elements in the system is represented by the constant phase angle element CPE. The equivalent circuit is represented by the parallel combination of the $R_b$ and CPE for each glassy sample [1, 30, 31].
Fig. 4.6. A impedance spectra for high conducting composition of SCV glassy samples at different temperatures.
Fig. 4.6. Impedance spectra for high conducting composition of SCV glassy samples at different temperatures.
Fig. 4.6. b Impedance spectra for high conducting composition of SCP glassy samples at different temperatures
Fig. 4.6. b Impedance spectra for high conducting composition of SCP glassy samples at different temperatures.
Fig. 4.6. c. Impedance spectra for high conducting composition of SCA glassy samples at different temperatures
Fig. 4.6. c. Impedance spectra for high conducting composition of SCA glassy samples at different temperatures
Fig. 4.7 Log(\(\sigma T\)) vs. 1000/T plots of various dopant compositions of a) SCV, b) SCP and c) SCA samples
Fig. 4.8 Activation energy for different various dopant compositions of a) SCY, b) SCP and c) SCA samples
4.2.2. Frequency Dependence of Conductivity

The ac conductivity is calculated from the measured real & imaginary parts of the impedance data and pellet dimensions for all the formers, modifier to formers & dopant compositions of the SCV, SCP & SCA (120 to 300K) and formers & modifier to formers compositions of SBS (300 to 473K) glassy samples. Fig. 4.9 a, b, c & d show respectively the frequency dependence of conductivity obtained at various temperatures for all the dopant compositions of SCV, SCP & SCA and modifier to former compositions of SBS glassy samples. From the fig 4.9 a, b, c & d, it is observed that the conductivity spectra show the two distinct regimes, within the measured frequency window, 1) plateau and 2) dispersive regions. The plateau region corresponds to frequency independent conductivity or known as dc conductivity. The $\sigma_0$ is obtained on extrapolation to lower frequencies and found to be in good agreement with the dc conductivity obtained from the impedance analysis. The frequency dependence of conductivity in the dispersive regions for all the compositions of the SCV, SCP, SCA & SBS samples at various temperatures were analyzed using the Universal Jonscher's power law.

$$\sigma_\omega = \sigma_0 + A \omega^s$$ \hspace{1cm} 4.37

The conductivity data were fitted to power law using non-linear regression procedure. From the analysis, the fitting parameters $\sigma_0$, A & s were obtained and table 4.1 gives $\sigma_0$ & s for the high conducting SCV, SCP, SCA & SBS samples. Fig. 4.10 a, b, c & d respectively show the temperature dependence of s for the dopant compositions of SCV, SCP & SCA and modifier to former compositions of SBS samples. Fig. 4.11 a, b, c & d show the $\log (\sigma/\sigma_0)$ vs. $\log (\omega/\omega_p)$ plots at various temperatures, where $\omega_p$ is the characteristic frequency at which $\sigma_\omega = 2\sigma_0$. 

92
Fig. 4.9 Log (φ) vs. log (ω) plots for the highest conducting dopant composition of a) SCV & b) SCP samples at different temperatures.
Fig. 4.9 Log (σ) vs. log (ω) plots for the highest conducting c) dopant composition of SCA & d) m/f composition of SBS samples at different temperatures.
Table 4.1. $s$, $\omega_p$ & $\sigma_0$ at temp [K] for high conducting SCV, SCP, SCA and SBS samples

<table>
<thead>
<tr>
<th>High conducting system</th>
<th>Temp [K]</th>
<th>$s$</th>
<th>$\omega_p$ (kHz)</th>
<th>$\sigma_0$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCV</td>
<td>168K</td>
<td>0.602</td>
<td>628</td>
<td>1.4883 x 10$^{-6}$</td>
</tr>
<tr>
<td>SCP</td>
<td>165K</td>
<td>0.643</td>
<td>371.5</td>
<td>2.6073 x 10$^{-6}$</td>
</tr>
<tr>
<td>SCA</td>
<td>168K</td>
<td>0652</td>
<td>94.2</td>
<td>1.7476 x 10$^{-7}$</td>
</tr>
<tr>
<td>SBS</td>
<td>413K</td>
<td>0.548</td>
<td>62.8</td>
<td>1.177 x 10$^{-7}$</td>
</tr>
</tbody>
</table>

In the fig. 4.9 a, b, c & d of $\log \sigma$ vs. $\log \omega$ plots, the frequency at which the dispersion region starts from the dc conductivity plateau can be defined as the characteristic frequency ($\omega_p$), where the relaxation effects of the ions occur. This characteristic frequency is termed as hopping rate ($\omega_p$) or cross over frequency and it occurs at $\sigma_o = 2\omega_o$ [24]. The relation between the dc conductivity and the hopping rate is given by $\sigma_o = k\omega_p$, where $k$ is the empirical constant, which depends on the concentration of mobile ions and details of the conduction mechanism. From the fig 4.9 a, b, c & d, it is observed that the dispersion region decreases with increase in temperature, where characteristic frequency $\omega_p$ shift towards the high frequencies, and disappears on further increase of temperature in the measured frequency window [32, 33]. The ion-hopping rate is less at low temperature as compared to that at high temperature. It is also found that the $\omega_p$ is thermally activated with the same energy as $\sigma_o T$.

In the fig. 4.10 a, b, c & d, the variation of $s$ with temperature can be related to the existence of distribution of relaxation parameters [34,35]. From the fig.4.11 a, b, c & d, the superimpossability of $\log (\sigma/\sigma_o)$ vs. $\log (\omega/\omega_p)$ at various temperatures suggests the conductivity relaxation mechanism is found to be temperature independent [36].
Fig. 4.10 $s$ as a function of temperature for the various dopant compositions of a) SCV, b) SCP & c) SCA and m/f compositions of d) SBS samples.
Fig. 4.11 Log $(\sigma/\sigma_0)$ vs. log $(\omega/\omega_p)$ plots for the highest conducting dopant composition of a) SCV and b) SCP samples at different temperatures.
Fig. 4.11 Log ($\sigma/\sigma_0$) vs. log ($\omega/\omega_p$) plots for the highest conducting c) dopant composition of SCA and d) m/f composition of SBS samples at different temperatures.
As observed in the conductivity spectra, the plateau region of conductivity may be due to transport of mobile ions in response to the applied electric field. The long-range transport of ion result in only successful jumps and their contribution yields d.c. conductivity ($\sigma_0$). The dispersive conductivity region with frequency can be explained with respect to the predicted theoretical Diffusion Controlled relaxation (DCR) model [35-37]. In this model, it is assumed that the glass forming matrix at the non-bridging oxygen (Si-O-, B-O-, V-O-, P-O- & As-O-) which is associated with a negatively charged ions to be a site and it can be doubly occupied by the cation (Ag$^+$). When a silver ion diffuses to a singly occupied site, the positions of the original ion on those sites excite and possess the higher energy configuration. At that time, the ions mutually rearrange within the region to achieve a new lowest energy site result in the former ion relaxation at that site is presumed to occur almost instantaneously. The excited ion can relax back to its original site or can diffuse to another adjacent site. This indicates the cation hopping and diffusion mechanism of the mobile silver ion at the local structures of the glass samples. The lower s value obtained from the power law expression can be correlated with the higher successful jumps, which result in the higher dc conductivity obtained for the former, m/f and dopant varied compositions of the SCV, SCP & SCA and former & m/f varied compositions of SBS samples.

4.2.3. Dielectric Permittivity Studies

From the measured $Z'$ & $Z''$ impedance data, $\varepsilon'$ real and $\varepsilon''$ imaginary parts the dielectric permittivity were calculated according to the equations 4.23 & 4.24 for all the formers, m/f & dopant compositions of SCV, SCP & SCA and formers & m/f compositions of SBS systems.

Fig. 4.12 a, b, c & d show the real part of dielectric permittivity $\varepsilon'$ vs. log f for the dopant compositions of SCV, SCP & SCA and modifier to former
Fig. 4.12 $\varepsilon'$ vs. log (freq) plots for the highest conducting dopant composition of a) SCV and b) SCP samples at various temperatures
Fig. 4.12 $\varepsilon'$ vs. log (freq) plots for the highest conducting c) dopant composition of SCA & d) m/f composition of SBS samples at various temperatures.
compositions of the SBS samples respectively. From the fig. 4.12 a, b, c & d, it is observed that with increase in frequency, \( \varepsilon' \) decreases and attains a constant value at high frequencies. At high frequencies, due to the high periodic reversal of the a.c field, there is no charge accumulation at the interface and hence the \( \varepsilon' \) remains constant, which can be explained in terms of the ion diffusion mechanism. At low frequencies, the charges get accumulated at the interfacial region that lead to a net polarization of the ionic medium result in the formation of space charge region at electrode-electrolyte interface which in turn increases the dielectric constant \( \varepsilon' \). [24, 38-42]. In \( \varepsilon'' \) vs. \( \log f \), the loss peak could not be observed in the measured frequency window and hence, the electric modulus formalism is used for further analysis.

### 4.2.4. Electric Modulus

The electric modulus data is calculated from the real & imaginary parts of the measured impedance data and pellet dimensions respectively using the equations 4.27 & 4.28 in section 4.1.3 for all the formers, m/f & dopant compositions of SCV, SCP & SCA and formers & m/f compositions of the SBS samples. The relaxation behavior is analyzed using the complex electric modulus \( (M^* = M' + jM'') \) formalism and the decay function \( \phi \) given by Kohlrausch-William-watts (KWW). Fig 4.13 a, b, c & d respectively show the imaginary part of electric modulus \( M'' \) vs. \( \log f \) for the high conducting dopant compositions of SCV, SCP & SCA samples and high conducting m/f compositions of SBS samples measured at various temperatures.

From the fig 4.13 a, b, c & d, it is observed that the shape of the curves are asymmetric with a long tail extending in the higher frequency region exhibiting non-Debye behavior and it also observed that the peak relaxation frequency, \( f_{\text{max}} \) shifts towards the higher frequency region with temperature. The \( M'' \) curves as a function of frequency were fitted to equation 4.31 using the
procedure of Moynihan et al. by a least square iterative software developed in Fortran 77 as discussed in section 4.1.3 for all the dopant compositions of SCV, SCP, SCA & m/f composition of SBS samples [21]. The initial parameters $M_s$, $\tau$ and $\beta$ are used in the fitting procedure to obtain the best fit. The $M_s$ value are obtained from the high frequency limit of the $M'$ vs. log $f$ plots. The $\tau$ & $\beta$ are the inverse of the peak relaxation frequency at $M''_{\text{max}}$ and the full width half maximum (FWHM) of the $M''$ vs. log $f$ curves respectively. The continuous lines represent the fitted values of $M''$, whereas the symbols represent the experimental data. The value of $\beta$ is graphically tuned such that the simulated modulus curve could be superimposed on the experimentally obtained modulus curves. Fig 4.14 a, b, c & d shows the temperature dependence of $\beta$ value for all dopant compositions of SCV, SCP & SCA & m/f compositions of SBS samples. Fig 4.15 a, b, c & d show the log $\tau$ vs. $1/T$ plots of all the dopant SCV, SCP & SCA and modifier to former compositions of SBS samples. The log $\tau$ vs. $1/T$ plots are fitted to

$$\tau = \tau_o \exp(E_r / kT)$$

by the linear least square fit and the relaxation activation energy is obtained from the slope of the fit. The obtained $E_r$, $\tau_o$, $f_{\text{max}}$ and $\beta$ values are given in table 4.2 for the high conducting composition SCV, SCP, SCA & SBS systems. Fig 4.16 a, b, c & d show the normalized $M''/M''_{\text{max}}$ vs. log $f/f_{\text{max}}$ obtained at different temperatures respectively for all the dopant compositions of SCV, SCP & SCA and m/f compositions of SBS samples.

According to the obtained results, the formers, modifier to formers & dopant compositions of SCV, SCP & SCA and former & m/f compositions of SBS samples, the $M''$ curves are related to the energy dissipation in the irreversible conduction process and they exhibit a non-exponential character of decay process.
Fig. 4.13 $M''$ vs. log (freq) plots for the highest conducting dopant composition of a) SCV and b) SCP samples at different temperatures.
Fig. 4.13 $M''$ vs. log (freq) plots for the highest conducting c) dopant composition of SCA & d) m/f composition of SBS samples at different temperatures.
Fig. 4.14 $\beta$ as a function of temperature for the various dopant compositions of 
a) SCV, b) SCP & c) SCA & m/f compositions of d) SBS samples
Fig. 4.15 Log (τ) vs. 1000/T plots for the various dopant compositions of
a) SCV, b) SCP & c) SCA & m/f compositions of d) SBS samples
Table 4.2. $\beta$ & $f_{\text{max}}$ at temp(K) and $E_r$ & $\tau_0$ for high conducting SCV, SCP, SCA and SBS samples

<table>
<thead>
<tr>
<th>High conducting System</th>
<th>Temp (K)</th>
<th>$\beta$</th>
<th>$f_{\text{max}}$ (kHz)</th>
<th>Relaxation activation energy ($E_r$)</th>
<th>$\tau_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCV</td>
<td>168K</td>
<td>0.68</td>
<td>44</td>
<td>0.3145±0.02</td>
<td>1.5523x10^{-13}</td>
</tr>
<tr>
<td>SCP</td>
<td>165K</td>
<td>0.54</td>
<td>70</td>
<td>0.232±0.01</td>
<td>1.642x10^{-13}</td>
</tr>
<tr>
<td>SCA</td>
<td>168K</td>
<td>0.6</td>
<td>5.89</td>
<td>0.2606±0.02</td>
<td>7.585x10^{-13}</td>
</tr>
<tr>
<td>SBS</td>
<td>413K</td>
<td>0.54</td>
<td>15.8</td>
<td>0.6212±0.03</td>
<td>9.562x10^{-13}</td>
</tr>
</tbody>
</table>

The broad non-Debye modulus spectra were interpreted in terms of distribution of relaxation times $\tau$, which in turn were related to the distributions of energy barriers $E_a$ [15, 36]. The $M''$ vs. log $f$ curves for all the samples showed a deviation over the simulated data at higher frequencies much larger than the peak frequency $f_{\text{max}}$, which could be explained by considering the contribution of asymmetric double well potential (ADWP) configuration to the conductivity [33, 43, 44]. From the above results, it could be concluded that the relaxation time $\tau$ is not a single valued, but is distributed over a mean value [40, 45].

From the fig. 4.13 a, b, c & d, with increase in temperature the broadness of the curves remain almost same, where $\beta$ remains almost constant would imply that all elements of the distributions have about the same activation energy. However, the shift in the $f_{\text{max}}$ with temperature could be explained based on the distribution of attempt frequencies for the barrier crossover or a distribution of jump or flight distances following the crossover. The broadness of the $M''$ vs. log $f$ curves is interpreted in terms of the distribution of relaxation times for distinguishable physical processes. Fig 4.14 a, b, c & d showed that the $\beta$ value is almost constant with temperature showing that the relaxation processes are temperature independent. The
Fig. 4.16 $M''/M''_{\text{max}}$ vs. log $(f/f_{\text{max}})$ plots for the highest conducting dopant composition of a) SCV and b) SCP samples at various temperatures.
Fig. 4.16 $M''/M''_{\text{max}}$ vs. $\log (f/f_{\text{max}})$ plots for the highest conducting c) dopant composition of SCA and d) m/f composition of SBS samples at various temperatures.
activation energies for the relaxation $E_r$ obtained from the slopes of the log $\tau$ vs. $1000/T$ plot in fig. 4.14 a, b, c & d are slightly higher than thermal activation energy, $E_a$. In the fig.4.16 a, b, c & d, the superimposability of normalized of $M''/M''_{\text{max}}$ vs. log ($f/f_{\text{max}}$) spectra revealed that the distribution of relaxation time is temperature independent.

Fig. 4.17a, b, c & d show the $Z''$ & $M''$ vs. log $f$ plots obtained at two different temperatures for the high conducting compositions of SCV, SCP & SCA and m/f compositions of SBS glassy samples respectively. From the fig 4.17 a, b, c & d, the observed broadening of $Z''$ and $M''$ spectra is due to the existence of a distribution of relaxation times of the intrinsically dispersive elements of the materials. The peak maxima of $Z''$ and $M''$ spectra do not coincide, as there exist a dispersion effect due to the distribution of relaxation times [46,47].

Fig 4.18 a, b, c & d show the $M''$ & log $\sigma$ vs. log $f$ plots obtained at two different temperatures for the high conducting composition of SCV, SCP & SCA and m/f compositions of SBS glassy samples respectively. From the fig 4.18 a, b, c & d, it is observed that the $f_{\text{max}}$ from the $M''$ vs. log $f$ modulus curve and the $\omega_p$ from log $\sigma$ spectra occur at the same frequency and with increase in temperature both $f_{\text{max}}$ & $\omega_p$ shifts to higher frequencies. The hopping rate $\omega_p$ with respect to the conductivity spectra and also the $f_{\text{max}}$ in the $M''$ plot could be a sensitive function of ion concentration and also may be due to some other material property [33]. As observed from the impedance, power law and modulus analysis respectively, the frequency at which the intersection occurs with real axis, the frequency at which relaxation effects begin and the peak relaxation frequency of $M''_{\text{max}}$, shift towards the higher frequencies with increase in temperature. From these observations, the conduction mechanism by which the Ag$^+$ ions preclude the matrix are correlated with ion hopping diffusion [48].
Fig. 4.17 Normalised $M''$ & $Z''$ vs. log (freq) plots for the highest conducting dopant composition of a) SCV & b) SCP samples at various temperatures
Fig. 4.17 Normalized $M''$ & $Z''$ vs. log (freq) plots for the highest conducting c) dopant composition of SCA & d) m/f ratio of SBS samples at various temperatures
Fig. 4.18 $M''$ & log ($\sigma$) vs. log (freq) plots for the highest conducting dopant composition of a) SCV & b) SCP samples at various temperatures
Fig. 4.18 M' & log (σ) vs. log (freq) plots for the highest conducting c) dopant composition of SCA & d) m/f ratio of SBS samples at various temperatures
4.3. CONCLUSIONS

The impedance measurements were made for all the formers, m/f & dopant compositions of the quaternary SCV, SCP & SCA samples at low temperature (120 to 300K) in the frequency range of 40Hz to 100kHz. The a.c. conductivity, dielectric permittivity and electric modulus were calculated from the measured real & imaginary parts of the impedance data and pellet dimensions, using their corresponding inter related formalisms. In the analyzed impedance spectra, with increase in temperature, the intersection of the semicircle with the real axis shifts towards the origin, in turn increase in conductivity. From the Arrhenius linear least square fit of the log (σT) vs. 1/T plot, the activation energy of the mobile charge carriers were calculated.

The conductivity with frequency dependence spectra were fitted to the Jonscher's power law expression and obtained the fit parameters σo, s & A. The obtained σo is in good agreement with the σdc. The conductivity spectral results are explained with the existing theoretical Diffusion Controlled Relaxation (DCR) model. The modulus spectra were fitted to the KWW decay function and obtained the stretched exponent β, the relaxation time τ and the shape of the spectra is non-Debye confirmed that the samples are ionic in nature. For various temperatures, the β value is found to be almost same. The superimpossability of the normalized M'' spectra at different temperatures were ascribed to temperature independent mechanisms of relaxation. The conductivity and the imaginary part of modulus M'' with a function of frequency compared & identified that the peak frequency fmax & the ωp occurs at the same frequency, which determines the material response in the vicinity of the conductivity relaxation time. The analysis by impedance, power law & modulus formalisms suggest that the Ag⁺ are the mobile cations & the mechanism by which they migrate are correlated with the DCR model to explain the ion hopping diffusion of Ag⁺ ions in the glassy matrix.
REFERENCES

1. J.Ross Macdonald
   (ed.), 'Impedance Spectroscopy',

2. J.F. Mccann, S.P.S. Badwal

3. B. Roling
   J. Non-Cryst. Solids, 244, (1999), 34

4. M. Le Stanguennec, S.R. Elliott
   Solid State Ionics, 73, (1994), 199

5. A.Hooper
   'Application of a.c. measurement and analysis techniques to
   materials research', AERE-R9757, (1980)

6. S.P.S.Badwal
   'Solid State Ionic Devices', Chowdari. B.V.R.

7. J.E.Bauerle

8. W.I Archer, R.D Armstrong
   'Electrochemistry', Chemical Soc.
   Specialist Periodical Reports, 6 (1978) 98

9. J. Ross Macdonald

    Solid State Commun. 35 (1980) 543

11. A.K.Jonscher
    b) J.Mater. Sci. 13 (1978) 553

12. J.C. Wang, J.B.Bates
    Solid State Ionics, 18-19 (1986) 224

13. R.D. Armstrong, M.F. Bell, A.A.Metcalf
    'Electrochemistry',Chemical Soc. Specialist Periodical Reports, 7 (1980) 157
14. Bernard A. Boukamp
   'Equivalent Circuit', University of Twente, (1989),
   Reports No. CT 128/88 / CT 112/89

15. L.L. Hench, J.K. West
   'Principles of Electronic Ceramics',

   J. Chem. Phys., 19, (1951), 1484

17. D.W. Davidson, R.H. Cole
   J. Chem. Phys., 19, (1951), 1484

18. S. Havriliak, S. Negami
    Polymer, 8, (1967), 161

    Phys. Chem. Glasses, 13, (1972), 171

    J. Am. Cream. Soc. 55, (1972), 492

    Phys. Chem. Glasses, 14, 6 (1973), 122

22. A.K. Joncher

23. A.K. Joncher

24. M.D. Ingram
    Phys. Chem. glasses, 28 (1987), 215

25. A.K. Joncher
    Nature, 267 (1977) 673

26. A.K. Joncher
    'Dielectric Relaxation in Solids',

27. R.J. Grant, M.D. Ingram, L.D.S Turner and C.A. Vincent
28. C. Chiodelli and A. Magistris  

29. Akira Doi  
   Solid State Ionics, 40 & 41 (1990) 262

30. Bernard A. Boukamp  

31. Bernard A. Boukamp, J.R. Macdonald  

32. H. Jain, O. Kanert  
   "Proceedings of the XII Int. Conf. on Defects in Insulating Materials".  

33. H. Jain, C.H. Hsieh  

34. H. Jain, J.N. Mundy  

35. A.H. Verhoeof, H.W. den Hartog  
   Solid State Ionics, 68 (1994) 305


37. S.R. Elliott, A.P. Owens  
   Philos. Magn. 60, 6 (1989) 777

38. C. Liu, C.A. Angell  


41. S.W. Martin, C.A. Angell  

42. F.S. Howell, R.A. Bose, P.B. Macedo, C.T. Moynihan  

44. K. L. Ngai, R. W. Rendell
   Handbook of conducting polymer vol. 2(ed).

45. S.W. Martin, C.A.Angell

46. D.P. Almond, A. R. West

47. D.P. Almond, A. R. West
   Solid State Ionics, 9 & 10 (1983) 277

48. J.C. Dyre
   Phys. Lett. 108A no. 9 (1985) 457