CHAPTER 4

ELECTRICAL PROPERTIES OF ZnO ADDED LITHIUM METASILICATE (Li$_2$SiO$_3$) CERAMICS
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The influences of addition of ZnO on structural, dielectric and electrical properties of Lithium metasilicate (Li$_2$SiO$_3$) ceramics has been investigated in this chapter.

4.1 SAMPLE PREPARATION

Lithium metasilicate (Li$_2$SiO$_3$) ceramics with different ZnO concentrations (i.e. 0.0, 0.1, 0.3 and 0.5 wt %) were prepared via solid-state reaction technique. The components Li$_2$CO$_3$ (99.9%), SiO$_2$ (99.9%) and ZnO (99.9%) were thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone medium for 1 h. The mixture was calcined at 900 °C for 4 h. The calcined powders were then pressed into cylindrical pellets of 12 mm diameter and 2-3 mm of thickness at a pressure of 80 MPa using a hydraulic press. PVA (poly vinyl alcohol) was used as a binder for preparing pellets. These pellets were, then, sintered at 900 °C for 2 h.

4.2 CHARACTERIZATION

4.2.1 X-ray diffraction

The XRD patterns of Li$_2$SiO$_3$ ceramic and ZnO added Li$_2$SiO$_3$ ceramics are compared in Figure 4.1 (a) and (b) respectively. All reflection peaks of XRD patterns were indexed in different crystal systems and unit cell configurations. Detailed analysis of the patterns exhibit that the samples have an orthorhombic structure with lattice parameters: $a = 9.396$ Å, $b = 5.396$ Å, $c = 4.661$ Å, which is in good agreement with the orthorhombic structure.
given in JCPDS card number 83-1517. For ZnO added Li$_2$SiO$_3$ ceramic (Fig. 4.1 (b)), it is clearly observed that minor trace of Lithium Zinc Silicate (JCPDS card number 24-0686) phase is observed. The average crystallite size was found to be 30 nm, 33 nm, 40 nm and 36 nm for 0.0, 0.1, 0.3 and 0.5 wt % ZnO added Li$_2$SiO$_3$ ceramics respectively.

**Fig. 4.1** Comparison of XRD patterns of (a) Li$_2$SiO$_3$ (b) ZnO added Li$_2$SiO$_3$ ceramics at room temperature
4.2.2 Microstructure analysis

Typical SEM micrographs of sintered samples are shown Fig. 4.2. The micrographs show the polycrystalline texture and the percentage of ZnO addition affects the microstructure. The highly distinctive, more or less uniform and compact grain distributions are observed. The grains grow and the size distribution becomes non-uniform at higher ZnO concentrations. The average grain size was found to be in the range of 1–3 μm, 0.7 - 2 μm, 0.5 – 1.3 μm and 0.5 – 1.4 μm respectively for 0.0, 0.1, 0.3 and 0.5 wt % ZnO added Li₂SiO₃ ceramics respectively.

Fig. 4.2 SEM micrographs of the samples with different ZnO contents (a) 0 wt %, (b) 0.1 wt %, (c) 0.3 wt %, (d) 0.5 wt %
4.3 DIELECTRIC SPECTROSCOPY

Fig. 4.3 (a) and (b) show the variation of dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) of all the samples with frequency at room temperature. It was observed that there is a decrease in $\varepsilon_r$ with increasing frequency for all the compositions indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons) [63]. The relative dielectric constant generally decreases on increasing ZnO concentration. The loss tangent (tan$\delta$) also decreases with increasing frequency. It is observed that at higher frequency, these parameters became almost frequency independent. From Fig. 4.3 (a) it is evident that 0.3 wt % ZnO added Li$_2$SiO$_3$ possesses low dielectric constant. The low dielectric constant provides an attractive feature for minimizing cross-talk and increasing signal transmission speeds. From Fig. 4.3 (b) it is evident that 0.3 wt % ZnO added Li$_2$SiO$_3$ also possesses low dielectric loss.

![Fig. 4.3](image)

**Fig. 4.3** Variation of relative dielectric constant ($\varepsilon_r$) (a) and loss tangent (tan$\delta$) (b) with frequency at room temperature for various ZnO contents

The temperature dependence of the relative dielectric constant ($\varepsilon_r$) of Li$_2$SiO$_3$ and ZnO added Li$_2$SiO$_3$ at selected frequencies ($10^3$, $10^4$, $10^5$ and $10^6$ Hz) is shown in Fig. 4.4. The broadening of dielectric peaks may be attributed to the disorder and defects present in the system. The peak value of dielectric constant ($\varepsilon_r$) of Li$_2$SiO$_3$ ceramic decreases with increase of ZnO concentration. It is interesting to note that peak was not observed in the
mentioned temperature range for 0.3 wt% ZnO added Li2SiO3 ceramic (Fig. 4.5(a)). The ZnO added Li2SiO3 ceramic is expected to have a lower dielectric constant at lower temperatures (≤ 200 °C) due to the immobile Zn2+ ions which block the movement of Li+ ions, but as the temperature increases, mobility of Li+ ions increases and raises the dielectric constant. At higher temperatures (> 200 °C), ZnO added Li2SiO3 ceramic has higher dielectric constant due to the polarizability of the Zn2+ ions (2.04 Å³), which are higher than those of Li+ ions (1.20 Å³). At 400 °C, the dielectric constant was found to be 263, 418, 277 and 364 for ZnO = 0.0, 0.1, 0.3 and 0.5 wt % at 1 kHz, respectively. The presence of high conducting Lithium zinc silicate phase in ZnO added Li2SiO3 ceramic may also be responsible for higher values of dielectric constant at higher temperatures (> 200 °C). If phases of different conductivity are present, motion of charge carriers occurs readily through one phase but is thwarted when it arrives at the boundary of another phase. This causes a build-up of a charge at the interface, which corresponds to a large polarization and high value of dielectric constant for ZnO added Li2SiO3 ceramics at higher temperatures (>200 °C). The charge accumulation at the grain boundaries is responsible for higher values of dielectric constant at low frequencies [64, 65]. At high frequency, ε results from the grains which have a small dielectric constant.

The dielectric loss is another parameter, which makes it possible to distinguish between samples of different compositions. The temperature dependence of the dielectric loss (tanδ) of Li2SiO3 and ZnO added Li2SiO3 shows that, generally, it increases faster above 280 °C (Fig. 4.4). This increase in tanδ may be due to enhancement in conductivity of the materials due to the movement of mobile (Li+) ions. The rapid increase of dielectric loss at higher temperature in low frequency region may be due to space charge polarization. It is found that the value of tanδ is very much dependent on temperature, frequency and concentration of ZnO. It was observed that the value of tanδ for 0.3 wt% ZnO added Li2SiO3 ceramic is smaller than that of its counterparts. Figure 4.5(b) shows the variation of tanδ from 30 °C to 200 °C at 100 kHz. The broadening of the peaks increases with the increase in the concentration of ZnO in Li2SiO3. For 0.3 wt% concentration of ZnO in Li2SiO3, no peak was observed in the studied temperature range. As the ZnO content increases, the value of tan δ decreases. However, the value of tanδ first decreases upto 0.3
wt% ZnO and then increases for 0.5 wt% ZnO added Li$_2$SiO$_3$ ceramic. It is evident that 0.3 wt% ZnO added Li$_2$SiO$_3$ ceramic is best in terms of dielectric loss. The high value of dielectric loss of 0.5 wt% ZnO added Li$_2$SiO$_3$ ceramic seems to be due to its high porosity as evident from the microstructure [Fig. 4.2(d)]. It is also interesting to observe that the dielectric loss at high frequencies is much lower compared to those at low frequencies. It shows the potential of using the material for high frequency applications with low dissipation factor. The addition of ZnO in Li$_2$SiO$_3$ is not expected to influence point defects in the materials as Zn$^{2+}$ and Li$^+$ has similar ionic size. When Zn$^{2+}$ is substituted at the Li$^+$ sites, there may be a change in the concentration of oxygen vacancies due to the variable oxidation states of both Zn and Li in Li$_2$SiO$_3$, explaining the decrease in dielectric constant and loss with an increase in ZnO concentration.
Fig. 4.4 Temperature dependence of $\varepsilon_r$ of Li$_2$SiO$_3$ ceramics with different ZnO contents 0.0, 0.1, 0.3 and 0.5 wt % at different frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz).

Fig. 4.5 Comparison of variation of (a) $\varepsilon_r$ and (b) $\tan\delta$ with temperature (30 °C – 200 °C) at 100 kHz for all the samples.
4.4 CONDUCTIVITY STUDY

The ac electrical conductivity for all the samples was calculated from the conductivity relation \( \sigma = \omega \varepsilon_0 \tan \delta \), where \( \varepsilon_0 \) is the vacuum permittivity and \( \omega \) is the angular frequency. Further the activation energy \( (E_a) \) was calculated from the \( \ln \sigma \) vs \( 10^3/T \) curve using the relation \( \sigma = \sigma_0 \exp \left(-E_a / K_B T\right) \), where \( K_B \) is the Boltzmann constant and \( \sigma_0 \) is the pre-exponential factor. Fig. 4.6 shows the variation of ac conductivity (\( \ln \sigma_{ac} \)) of the materials as a function of inverse of absolute temperature \( (10^3/T) \) at three different frequencies.

![Fig. 4.6 Temperature-frequency dependence of ac conductivity of the samples with different ZnO contents](image)

Fig. 4.6 Temperature-frequency dependence of ac conductivity of the samples with different ZnO contents (a) 0 wt %, (b) 0.1 wt %, (c) 0.3 wt % and (d) 0.5 wt %

It is observed that the ac conductivity of the materials increases with rise in temperature, and shows the negative coefficient of resistance behavior. The nature of variation of \( \sigma_{ac} \)
over a wide temperature range supports the thermally activated transport properties of the materials. The values of $E_a$ for all compositions at different frequencies are given in Table 4.1. The value of activation energy of the samples in the region (I) which is found to be very low ($<< 1$ eV) confirms the presence of electronic nature of conduction process. It is due to the electron hopping between the ions of different valances. The values of $E_a$ for all the compositions in region (II) are ascribed to the motion of $\text{Li}^{+}$ ions and oxygen ion vacancies [69]. The activation energy was found to increase with increasing temperature. This behavior suggests that the conduction mechanism in the samples may be due to hopping of charge carriers. Table 1 show that the activation energies of the samples in region (II) decrease gradually with increasing frequencies. The $E_a$ values of 0.3 wt % ZnO added Li$_2$SiO$_3$ ceramic in region (II) is found to be smaller than that of its counterparts. When Zn$^{2+}$ is substituted at the Li$^{+}$ sites, there may be a change in the concentration of oxygen vacancies due to the variable oxidation states of both Zn and Li in Li$_2$SiO$_3$. With increase in ZnO concentration, there may be an increase in oxygen vacancies leading to an increase in the number of conduction electrons. So activation energy decreases with an increase in ZnO concentration. This change in behavior indicates the participation of Zn ions in the relaxation and conductivity processes. Again the strong increase in the dielectric characteristics with increasing temperature may be due to thermally induced oxygen ion vacancies and enhancement of hopping conduction.
Table 4.1: Comparison of activation energies $E_a$ (in eV) of Li$_2$SiO$_3$ ceramic for different ZnO concentrations at 10 kHz, 100 kHz and 1 MHz

<table>
<thead>
<tr>
<th>Frequency</th>
<th>ZnO content (wt %)</th>
<th>Region I ($E_a$ in eV)</th>
<th>Region II ($E_a$ in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 kHz</td>
<td>0.0</td>
<td>0.059</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.126</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.019</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.037</td>
<td>0.90</td>
</tr>
<tr>
<td>100 kHz</td>
<td>0.0</td>
<td>0.053</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.109</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.053</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.055</td>
<td>0.75</td>
</tr>
<tr>
<td>1 MHz</td>
<td>0.0</td>
<td>0.070</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.118</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.085</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.057</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### 4.5 IMPEDANCE PROPERTIES

The complex impedance Spectroscopy (CIS) technique [66] was used to study the electrical response (i.e., transport properties) of polycrystalline samples in a wide range of frequencies ($10^2$ - $10^6$ Hz). This technique enables us to separate the real and imaginary components of the complex impedance parameters, and hence provides information of the structure – property relationship of the sample. A polycrystalline material usually has grain and grain boundary properties with different time constants at high temperature leading to two successive semicircles. It can conventionally be displayed in a complex plane plot (Nyquist diagram) in terms of the following formalism:

Complex impedance, $Z^* (\omega) = Z' - jZ''$  \[4.1\]

where $Z' = |Z| \cos \theta$ and $Z'' = |Z| \sin \theta$
Fig. 4.7 Complex impedance plots, $Z'$ vs $Z''$ at different temperatures for (a) 0.0 wt% (b) 0.1 wt% (c) 0.3 wt% and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ ceramic with corresponding equivalent circuit [inset]
Figure 4.7 shows complex impedance plots \((Z' \text{ vs } Z'')\) of ZnO added Li\(_2\)SiO\(_3\) ceramics at different temperatures over a wide range of frequency (100 Hz – 5 MHz). The impedance plot of all the samples shows depressed semicircular arcs whose center lies below the real axis. The effect of ZnO addition in the impedance plots of Li\(_2\)SiO\(_3\) ceramic is clearly seen in Fig. 4.7. A single semicircular arc has been observed at 250 °C and at higher temperatures (≥300 °C), two overlapping semicircles are clearly seen for 0.0 and 0.5 wt% concentration of ZnO in Li\(_2\)SiO\(_3\) whereas 0.1 and 0.3 wt% ZnO added Li\(_2\)SiO\(_3\) ceramic shows single semicircular arcs up to 300 °C and two semicircles with different values of resistance for bulk \((R_b)\) and grain boundary \((R_{gb})\) at temperatures (≥350 °C). The nature of the plots corroborates the existence of non-Debye and polydispersive relaxation process.

Each semicircle is a representative of an RC circuit that corresponds to individual component of the materials (Fig. 4.7 [inset]). From the graph it is evident that as the temperature increases intercept along the real \((Z')\) axis shifts towards the origin indicating the increase in conductivity of the samples. The impedance data were analyzed in order to obtain the bulk resistance \((R_b)\), grain boundary resistance \((R_{gb})\), bulk capacitance \((C_b)\) and grain boundary capacitance \((C_{gb})\) of the samples. The values of \(R_b\) and \(R_{gb}\) can be obtained from the intercept on the \(Z'\)-axis, the variation of which with ZnO concentration at 400 °C is shown in Fig.4.8 (a). It is clear from Fig. 4.7 that the value of \(R_b\) decreases with the increase in temperature, which evidently shows the NTCR behavior of all the samples. It is evident from Fig. 4.8(a) that both the bulk and grain boundary resistances decrease with an increase in ZnO concentrations and is found to be smallest for 0.3 wt% ZnO added Li\(_2\)SiO\(_3\) ceramic. Hence we can conclude that the effect of ZnO in Li\(_2\)SiO\(_3\) ceramic brings the grain and grain boundary resistance to of almost the same order of magnitude and it helps in decreasing the grain and grain boundary resistances.

The capacitances \((C_b\text{ and } C_{gb})\) can be calculated using the relation:

\[
\omega_{\text{max}}RC = 1 \quad 4.2
\]

where \(\omega_{\text{max}} (=2\pi f_{\text{max}})\) is the angular frequency at the maxima of the semicircle. Fig. 4.8(b) shows the variation of \(C_g\) and \(C_{gb}\) with ZnO concentration at 400 °C. The ratio between the grain boundary capacitance and grain capacitance is very high for all samples. This suggest
that the grain boundary plays a significant role in deciding the dielectric properties of all ZnO added Li$_2$SiO$_3$ ceramics.

Fig. 4.8 Variation of (a) $R_b$, $R_{gb}$ and (b) $C_b$, $C_{gb}$ with ZnO concentration at 400 °C

Fig. 4.9 Variation of imaginary part of impedance ($Z''$) as a function of frequency of (a) 0.0 wt% (b) 0.1 wt% (c) 0.3 wt% and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ at three different temperatures
Figure 4.9 represents the impedance loss spectrum (i.e., variation of imaginary part of impedance $[Z'']$ with frequency) of all the samples at three different temperatures. The curves show that the value of $Z''$ reaches maximum value of $Z''_{\text{max}}$ at all temperatures. For the temperature below 300 °C, the peak was beyond the range of frequency measurement. The frequency of the maximum, shifts to its higher value on increasing temperature. This behavior suggests the presence of hopping type mechanism in the samples. Also, as the temperature increases the magnitude of $Z''$ decreases, the effect being more prominent at the peak position. For all the samples, it is observed that peak broadening increases with a rise in temperature. The clear shift in the peak towards higher frequency with a rise in temperature is due to the decrease in the bulk resistivity of the samples. The asymmetric peaks imply the existence of electrical processes in the samples with spread of relaxation time and deviation from ideal Debye-like behavior. The merging of $Z''$ values in the high frequency region might be an indication of the buildup of space charge in the samples. The effect of increase of ZnO concentration on the electrical behavior of the samples can clearly be seen in terms of increase in the magnitude of $Z''$, peak broadening and asymmetry.

The most probable relaxation time ($\tau$) can be determined from the position of the loss peak in the $Z''$ or $M''$ versus ln($f$) plots according to the relation: $\tau = 1/2\pi f_{\text{max}}$, $f$ is the relaxation frequency. The variation of $\tau$ as a function of inverse of absolute temperature of all the samples at high temperature region is shown in Fig. 4.10. The $\tau$-values of all the samples are found to be decreasing on increasing temperature, which is a typical semiconductor behavior. The graph follows the Arrhenius relation, $\tau = \tau_0 \exp (-E_a/K_B T)$ (where $\tau_0$ pre-exponential factor, $E_a$ activation energy, $K_B$ Boltzmann constant and $T$ absolute temperature). The relaxation time is thermally activated process and the activation energy values of the samples are found to be in the range of 1.28 eV to 1.53 eV. With the help of modulus plot, variation of most probable conduction relaxation time ($\tau$) with temperature is shown in Fig. 4.10 [inset]. The values of the activation energy obtained from the slope of ln ($\tau$) against $10^3T^{-1}$ curve are found to be in the range of 0.55 eV to 0.76 eV which is similar to those for ionic conductivity and oxygen vacancy migration. $E_a$ values obtained from the $Z''$ spectra represent the localized conduction (i.e., dielectric relaxation) and those of $M''$ spectra represent nonlocalized conduction (i.e., long range conduction). It
is clear that the activation energy of the compounds (calculated from loss and modulus spectrum) is different and this suggests that the nature of species taking part in both localized and nonlocalized conduction is different.

**Fig. 4.10** Variation of relaxation time with $10^3/T$ of (a) 0.0 (b) 0.1 (c) 0.3 and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ calculated from $Z''$ with frequency and $M''$ with frequency (inset)
4.6. MODULUS STUDIES

Fig 4.11 shows the variation of $M''$ with frequency for all the samples at three different temperatures. Peaks of $M''$ that appeared up to 400 °C in the high frequency range for all the samples are originating from the grains and those from the grain boundaries do not appear because of very high grain boundary capacitance ($C_{gb}$). It is evident from the spectra that the grain relaxation takes place in the same frequency range, irrespective of the addition of ZnO suggesting that relaxation time ($\tau$) is nearly the same for all the three samples (i.e., 0.1, 0.3, 0.5 wt % ZnO added Li$_2$SiO$_3$). As, the difference in peak heights of the three samples is insignificant, it is suggestive in a gross way that the true lattice responses of all the samples remain unchanged despite differences in their effective dielectric constant. The value of $M''$ for all the samples increases as a function of temperature. In all the cases, the relaxation peaks shift towards higher frequency side with rise in temperature. The Li$^+$ ions can drift to long distances in the frequency range that is below $M''$ peak position. In the frequency range which is above that of the $M''$ peak, the ions are spatially confined and free to move inside their potential wells. The region of the peak therefore is indicative of the transition from long range dominated to short range dominated mobility. The asymmetric peak broadening indicates the spread of relaxation times with different time constant, and hence relaxation is of non-Debye type.

![Graphs showing variation of $M''$ with frequency for different temperatures](image)
Fig. 4.11 Variation of imaginary part of modulus ($M''$) with frequency of (a) 0.0 wt% (b) 0.1 wt% (c) 0.3 wt% and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ at selected temperatures.

Fig. 4.12 Variation of $M'$ with frequency of (a) 0.0 wt% (b) 0.1 wt% (c) 0.3 wt% and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ at selected temperatures.
Fig 4.12 shows the variation of $M'$ with frequency for all the samples at three different temperatures. A very low value (~zero) of $M'$ in the low frequency region is observed suggesting the suppression of electrode effect in the materials. The value of $M'$ decreases with rise in temperature in the high-frequency region. Continuous increase was observed in the dispersion with increasing frequency at all temperatures. Such observations could possibly be related to a lack of restoring force governing the short range mobility of the charge carriers under the action of an induced electric field [70].

![Graphs showing variation of $M'$ with frequency](image)

**Fig. 4.13** Variation of normalized $Z''$ and $M''$ with frequency for (a) 0.0 wt% (b) 0.1 wt% (c) 0.3 wt% and (d) 0.5 wt% ZnO added Li$_2$SiO$_3$ at 400 °C
Fig. 4.13 shows the variation of scaled parameters \( (Z''/ Z''_{\text{max}} \text{ and } M''/ M''_{\text{max}}) \) versus frequency for all the samples at 350 °C. It can be observed that the peaks are not occurring at the same frequency \( (f_{Z''} < f_{M''}) \) for different ZnO concentrations. Although ZnO has been added, the mismatch among the peaks of \( Z''/ Z''_{\text{max}} \) and \( M''/ M''_{\text{max}} \) frequency plot are observed for all compositions. The existence of an appreciable separation between these peaks suggests the presence of localized movement of charge carriers (via hopping type mechanism) and deviation from an ideal Debye-like behavior for all samples. The decrease of \( R_b \) values in all samples with the rise in temperature is indicative of the presence of long range conductivity in all samples. The separation between the peaks of \( Z''/ Z''_{\text{max}} \) and \( M''/ M''_{\text{max}} \) frequency plot is less for 0.3 wt% concentration of ZnO in Li\(_2\)SiO\(_3\) ceramic. Thus, 0.3 wt% ZnO added Li\(_2\)SiO\(_3\) ceramic, with its smaller values of \( R_b \) has a greater long range conductivity compared to other samples.

The scaling behavior of the samples were studied by plotting \( M''/ M''_{\text{max}} \text{ vs. } \log_{10} (f/f_{\text{max}}) \) at selected temperatures and is shown in Fig. 4.14 where \( f_{\text{max}} \) is the frequency corresponding to \( M''_{\text{max}} \). It is observed that for all compositions, the \( M'' \) spectra at different temperatures do not merge into a single master curve. This deviation from the single master curve of the scaling behavior clearly indicates that the dynamical processes are temperature dependent in all the samples. It is observed that all the peaks are asymmetric in position (lying in the dispersion region of \( M' \text{ vs. } f \) pattern) and asymmetric peaks move in the direction of higher frequency sides on increasing temperature. The low frequency side of the peak in \( M''/ M''_{\text{max}} \text{ vs. } \log_{10} (f/f_{\text{max}}) \) curve corresponds to the range in which the charge carriers can drift to long distance (i.e., charge carriers can perform successful hopping from one site to the neighboring site). In the high frequency range, the charge carriers are spatially confined to their potential wells, and thus could make localized movements inside the well. The region where peak occurs is an indicative of the transition from the long range to the short range mobility with increase in frequency.
4.7 FREQUENCY DEPENDENCE OF AC CONDUCTIVITY

The frequency dependence of ac conductivity, $\sigma (\omega)$, at various temperatures for all the samples is shown in Figure 4.15. The conductivity increases with rise in frequency, which is a characteristic of $\omega^n$ ($n =$ exponential). The decrease in bulk resistance of all the samples with increase in temperature is also evidenced in the plot since the conductivity increases with rise in temperature. The conductivity dispersion, suggests that the electrical conduction of the compounds is a thermally activated process which obeys the Jonscher’s universal law, $\sigma_{ac} = \sigma_0 + B\omega^n$, where $\sigma_0$ is the dc conductivity at a particular temperature, $B$
is the temperature dependent constant and \( n \) is the frequency exponent which generally lies between 0 and 1. The exponent \( n \) represents the degree of interaction between the mobile ions. According to Jonscher, the origin of frequency dependence of conductivity lies in the relaxation phenomenon arising due to mobile charge carriers. The low frequency dispersion has been attributed to the ac conductivity whereas the frequency independent plateau region of the conductivity pattern corresponds to dc conductivity of the materials. The temperature, at which grain resistance dominates over grain boundary resistance, is marked by a change in the slope of ac conductivity with frequency. The frequency at which the change of slope takes place is known as the hopping frequency \( (\omega_p) \). The hopping frequency shifts to higher frequency side with rise in temperature. The charged species that have been accumulated at the grain boundaries have sufficient energy to jump over the barrier on increasing temperature. The variation in exponent \( n \) as a function of temperature is represented in Fig. 4.16. It is known that the conductivity mechanism in any material could be understood from the temperature dependent behavior of \( n \). To determine the electrical conduction mechanism in the materials, various models have been proposed [71]. These models include quantum mechanical tunneling (QMT) model, the overlapping large-polaron tunneling (OLPT) model, and the correlated barrier hopping (CBH) model. According to the QMT model, the value of exponent \( n \) is found to be 0.8 and increases slightly with an increase in temperature, whereas OLPT model predicts the frequency and temperature dependence of \( n \). In the CBH model, the temperature dependent behavior of \( n \) is proposed. This model states the charge transport between localized states due to hopping over the potential barriers and predicts a decrease in the value of \( n \) with increase in temperature, which is consistent with the behavior of \( n \) for the samples under study (Fig. 4.16). This suggests that the conductivity behavior of ZnO added Li_2SiO_3 ceramics can be explained using the CBH model.
Chapter 4

Fig. 4.15 Variation of ac conductivity of samples with frequency at different temperatures

Fig. 4.16 Variation of $n$ as a function of temperature for all the samples
4.8 CONCLUSIONS

The polycrystalline ZnO added Lithium metasilicate (Li$_2$SiO$_3$) ceramics were prepared through solid state reaction technique. The dielectric constant and the dielectric loss decrease significantly as the ZnO concentration increases. Samples generally showed a gradual decrease in dielectric constant and dielectric loss with increase of the frequency. Complex impedance-spectroscopic study of the sample reveals that the electrical processes in the material are due to both bulk and grain boundary whereas the contribution of electrode effect is ineffective. Moreover, two conduction mechanisms were identified: a dielectric relaxation processes due to localized conduction associated with the presence of oxygen vacancy and the nonlocalized conduction corresponding to long range conductivity associated with extrinsic mechanisms due fundamentally to, Li$^+$ presence. Three conductivity components were recognized inside the grain: dc conductivity at low frequency region, a capacitive behavior at higher frequencies, and a universal power law behavior in an intermediate-frequency region. The AC conductivity of the systems has been studied by means of complex impedance spectroscopy. From the dielectric studies, we may prescribe 0.3 wt % ZnO added Li$_2$SiO$_3$ sample as a good dielectric material since it possesses low dielectric constant and low tangent loss. The activation energies of all the samples at higher temperatures were found to be less than 1 eV. This suggests the presence of singly ionized oxygen vacancies in the conduction process. The relaxation time, $\tau$, also shows Arrhenius behavior and the values of activation energy, $E_a$ of the compounds (obtained from loss and modulus spectrum) are different and this suggests that the nature of species taking part in both localized and nonlocalized conduction is different. Temperature dependent behavior of the frequency exponent ($n$) suggests that the correlated barrier hopping model is most likely to rationalize the electrical transport phenomenon in ZnO added Li$_2$SiO$_3$ ceramics. Moduli plots do not collapse on to master plots suggesting the absence of common charge transport mechanism in these ceramics.