EXPERIMENTAL TECHNIQUES

The present investigation comprises the following two parts:

1. The synthesis of NASICON phosphate glasses of various compositions.
2. Characterization, physical, thermal and electrical studies of the prepared glasses.

2.1 Preparation of glasses

In principle any substance can be made into a glass provided it is cooled from its liquid state fast enough to prevent crystallization [1, 2]. In actual practice, glass formation has been achieved with relatively limited number of substances. There are at least a dozen of different techniques used to prepare materials in an amorphous state. Three commonly used methods are: (i) melt quenching, (ii) thermal evaporation, and (iii) sol-gel process. The first method speeds up the rate of cooling from the liquid state by employing the different sophisticated techniques, with a quenching rate of $10^9$ K/s [3,4]. The second method involves the condensation of the vapor phase to the glassy thin films. In the third method glass materials are obtained by sol-gel process [5]. In this, melt quenching is the oldest method of producing an amorphous solid in which the molten form of the material is cooled quickly to stop the crystal growth [6]. There are several techniques that can be used to prepare glassy materials using melt quenching method. Out of these, five are commonly used to prepare most of the non-crystalline materials for commercial or academic. Quenching rates play a significant role in the preparation of glassy solids. Different quenching rates are categorized by:

a. Slow quenching (cooling rate $\sim 10$ K/s)
b. Moderate quenching (cooling rate $\sim 10^2$ K/s)
c. Rapid splat quenching (cooling rate $\sim 10^5$ K/s)
d. Condensation from vapor (cooling rate $\sim 10^8$ K/s)
Fig. 2.1: Different methods of glass preparation: (a) Twin roller quenching (b) melt spinning (c) Slow cooling of the melt, (d) Quenching of the melt in liquid nitrogen and (e) Thermal evaporation.
Different methods of preparation of glassy solids are schematically shown in Fig. 2.1. For materials with very high glass forming tendency like SiO$_2$, the melt can be allowed to cool slowly at the rate of $10^{-4}$ to $10^{-1}$K/s by simply turning off the furnace or by bringing down its temperature in a programmed manner. For example, 1K/s is being used to form an amorphous solid of glass formers such as SiO$_2$, B$_2$O$_3$ or P$_2$O$_5$. Some materials require faster cooling rates and these materials are prepared by quenching the melt in air or in water, in this case the rate of cooling would be in the range of $10^1$-$10^2$K/s. Metallic glasses require a very high cooling rate ~ $10^5$ to $10^6$ K/s which can be obtained by splat-quenching method in which a material in its molten form is poured into the gap between two mutating rollers [7, 8]. Another method to obtain an amorphous solid is by by-passing the liquid state completely using vacuum thermal evaporation, sputtering decomposition of gaseous compound by r-f discharge, or deposition from salt solution by electrolysis [9].

In the present investigation vitreous samples of NASICON phosphate with various compositions were synthesized by melting the mixture of stoichiometric quantities of raw materials and they are shown in Table 2.1. The overall reaction for the formation of Na$_5$TiP$_3$O$_{12}$, Li$_5$Nb$_{1-x}$Zn$_{2.5x}$P$_3$O$_{12}$ (where $0 \leq x \leq 0.4$) and Ag$_4$NbP$_3$O$_{12}$ are given by:

$$2.5\text{Na}_2\text{CO}_3 + \text{TiO}_2 + 3\text{NH}_4\text{H}_2\text{PO}_4 \xrightarrow{\Delta} \text{Na}_5\text{TiP}_3\text{O}_{12} + 3\text{NH}_3 + 9/2\text{H}_2\text{O} + 2\text{CO}_2$$

$$5/2\text{Li}_2\text{CO}_3 + x/2\text{Nb}_2\text{O}_5 + (5x/2)\text{ZnO} + 3\text{NH}_4\text{H}_2\text{PO}_4 \xrightarrow{\Delta} \text{Li}_5\text{Nb}_{1-x}\text{Zn}_{2.5x}\text{P}_3\text{O}_{12} + 3\text{NH}_3 + 9/2\text{H}_2\text{O} + 5/2\text{CO}_2$$

$$4\text{AgNO}_3 + ½ \text{Nb}_2\text{O}_5 + 3\text{NH}_4\text{H}_2\text{PO}_4 \xrightarrow{\Delta} \text{Ag}_4\text{NbP}_3\text{O}_{12} + 4\text{NO}_2 + 3\text{NH}_3 + 9/2\text{H}_2\text{O} + \text{O}_2$$

Similar reaction condition was followed for the preparation of other samples. The synthetic procedure was optimized by varying the choice of reagents, heating temperature and duration of reaction. The following is the typical procedure for the preparation of samples:
**Step 1:** The calculated amounts of the starting materials were weighed and ground in an agate mortar for 45 min.

**Step 2:** The mixture was placed in silica crucible and slowly heated in an electrical furnace up to 573 K for 6 hours in order to ensure the total decomposition of the reagents. For silver based samples the mixture was maintained at 443 K for 48 hours for the decomposition of the reagents.

**Step 3:** After cooling to room temperature, the mixture was again ground for 45 min in agate mortar and heated in a silica crucible for 14-16 hours at temperature 673-1073 K depending upon the composition without melting the mixtures.

**Step 4:** The samples were heated further to melting and stirred for 5-10 min to ensure homogeneity.

**Step 5:** Finally, the melts were poured into stainless steel plate and quenched by pressing with another stainless steel plate at room temperature. Stainless steel plates were preheated before quenching for some of the samples to get a brittle less glass.

**Step 6:** Soon after the glass preparation, the glass samples are kept for annealing well below the glass transition temperature in order to avoid internal mechanical stresses developed during solidification of liquid phase to glassy phase.

**Table 2.1: Glass Compounds prepared and the starting materials used**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Glass Compound</th>
<th>Starting materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$A_4$NbP$<em>3$O$</em>{12}$ ($A = \text{Na, Li, Ag}$), $A_5$TiP$<em>3$O$</em>{12}$ ($A = \text{Na, Li, Ag}$), $A_{(4+x)}$Ti$<em>x$Nb$</em>{(1-x)}$P$<em>3$O$</em>{12}$, where $A = \text{Li, Na (0.0≤x≤1.0)}$.</td>
<td>Na$_2$CO$_3$, Li$_2$CO$_3$, AgNO$_3$, TiO$_2$, Nb$_2$O$_5$, NH$_4$H$_2$PO$_4$.</td>
</tr>
<tr>
<td>2.</td>
<td>$(\text{Li}<em>x\text{Na}</em>{1-x})_4$NbP$<em>3$O$</em>{12}$, $(\text{Li}<em>x\text{Na}</em>{1-x})_5$TiP$<em>3$O$</em>{12}$.</td>
<td>Na$_2$CO$_3$, Li$_2$CO$_3$, TiO$_2$, Nb$_2$O$_5$, NH$_4$H$_2$PO$_4$.</td>
</tr>
<tr>
<td>3.</td>
<td>$A_2$NbMP$<em>3$O$</em>{12}$, where $A=\text{Li, Na and M=Cu, Zn, Cd, Pb}$, $A_4$Nb$<em>{(1-x)}$Zn$</em>{5x}$P$<em>3$O$</em>{12}$.</td>
<td>Na$_2$CO$_3$, Li$_2$CO$_3$, Nb$_2$O$_5$, NH$_4$H$_2$PO$_4$, CuO, ZnO, CdO and PbO</td>
</tr>
</tbody>
</table>
2.2 Physical Characterization

2.2.1. X-Ray Diffraction

X-Ray diffraction (XRD) technique has been an indispensable tool for structural studies of solids [10]. It gives a complete description of the structure such as the crystal system, space group, unit cell dimension, atomic coordinates and electron density distribution around them [11]. There are three standard methods of X-ray diffraction analysis for the crystal structure determination:

1. Laue method
2. Rotating crystal method
3. Powder method

Fig. 2.2: XRD pattern of Li_{(4+x)}Ti_{x}Nb_{(1-x)}P_{3}O_{12} (LNTP_x) where 0≤x≤1 with no characteristic peaks.

In the present study the powder method has been used, in which the incident monochromatic radiation are allowed to fall on a finely powdered specimen. The diffracted rays leave individual crystallites satisfying the Bragg's equation, \(2d \sin \theta = n \lambda\), where \(\lambda\) is the wavelength of the monochromatic X-ray, \(n\) is the order of the diffraction, \(d\) is the perpendicular distance between the parallel planes in the crystal and \(\theta\) is the angle of diffraction. The XRD measurements usually yields structure less peaks for amorphous materials due to its disorder. In the present study XPert PANalytical X-ray diffractometer
with monochromatic CuK\(_\alpha\) radiation (\(\lambda=1.5418\) Å) was employed to record on powder glass samples at room temperature. The scanning was made at the rate of 2°/min at the glancing angles between 5 and 75°. Fig. 2.2 shows the XRD pattern of Li\(_{(4+x)}\)Ti\(_x\)Nb\(_{1-x}\)P\(_3\)O\(_{12}\) (LNTP\(_x\)), where 0\(\leq x\leq 1\). It didn’t show any characteristic peak intimating the amorphous nature of the sample. The similar nature was observed for all the samples prepared.

### 2.2.2 Density Measurement

Density of the freshly synthesized bulk glassy samples can be used to characterize glasses. The relation between density and composition is very important because of its association with the structural details of the glass. Density changes may occur in a glass by changing the composition of the glass formers or the glass modifiers. Minami and Tanka [12] have calculated the molar volume and ion concentration in silver ion conducting glasses from the measured density. Calvo and Jordan [13] reviewed the observed density and proposed a structural model to explain the variation of density with composition. The density measurements were also used to find the oxygen packing density in oxide glasses [14]. In the present study density of the glasses were determined by Archimede’s method using glass fragments free from bubbles. High purity xylene was used as buoyancy liquid and a single pan electrical balance of 10\(^{-4}\) g sensitivity was used to measure the weight of the liquid and the glass samples. The density is obtained from the relation:

\[
\rho = \frac{W_a \rho_1}{(W_a - W_1)},
\]

where \(\rho\) is the density of the sample, \(W_a\) is the weight of the sample in air, \(W_1\) is the weight of the sample fully immersed in liquid and \(\rho_1\) is the density of the liquid used. These measurements were carried out at room temperature with an accuracy of ±0.03g/cm. The molar volume \(V_m\) was calculated from density using formula \(V_m = M/\rho\), where \(M\) is the corresponding molecular weight of the samples.

### 2.2.3 Thermal Analysis

Measurement of physical and chemical properties of the materials as a function of temperature is called the thermal analysis. Thermal analysis techniques are useful to determine the glass transition temperature, chemical decompositions, phase transition
temperature, crystallization kinetics of glass and polymers, coefficient of thermal expansion and heat capacity, etc. The differential scanning calorimetry (DSC) is a versatile technique to study phase transitions such as glass transition temperature $T_g$, onset of the crystallization temperature $T_s$, crystallization temperature $T_c$, and melting temperature $T_m$ of the glass. In this technique, the sample and the reference material are maintained at the same temperature during the heating process. The extra heat input required to maintain the temperature during the event in the sample is measured and plotted against temperature or time. During the thermal event, the sample temperature either lags behind or leads the temperature of the reference depending on the change whether it is endothermic or exothermic.

Fig 2.2: DSC thermogram of Li$_5$TiP$_3$O$_{12}$ glass sample in N$_2$ flow at 10$^\circ$C/min heating rate showing $T_g$ is glass transition temperature, $T_s$ is onset crystalline temperature, $T_c$ is crystalline temperature and $T_m$ is melting temperature.
The thermal stability $\Delta T$ parameter is usually employed to estimate the glass stability [15] which is defined by:

$$\Delta T = T_s - T_g$$  \hspace{1cm} (2.2)

According to Saad and Poulin [16] the thermal stability parameter $S$ which reflects the resistance for devitrification of glass and it is defined by:

$$S = (T_c - T_s) / (T_c - T_g)$$  \hspace{1cm} (2.3)

The term $(T_c - T_s)$ is the rate of devitrification transformation of glassy phase. The glass forming ability parameter $K_{gl}$ known as Hruby’s parameter for the different glass is given by [17]:

$$K_{gl} = (T_c - T_g) / (T_m - T_c)$$  \hspace{1cm} (2.4)

The value of $\Delta T$, $S$ and $K_{gl}$ calculated from Eqs. (2.2), (2.3) & (2.4) respectively and these are used later and the results are discussed subsequently. According to Hruby, higher the value of $K_{gl}$ greater its stability against crystallization and supposedly the higher the vitrification ability. The DSC studies were carried out using thermal analyzer TA-SDT-Q600 in temperature range 313–1173K and Mettler Toledo 821 in the temperature range 313–773K instruments under N$_2$ atmosphere at a heating rate of 10 K min$^{-1}$ on the as-quenched glass-plate. Fig 2.2 shows the DSC thermogram of Li$_5$TiP$_3$O$_{12}$ glass sample showing glass transition temperature $T_g$, onset crystalline temperature $T_s$, crystalline temperature $T_c$ and melting temperature $T_m$.

### 2.3.4 Fourier Transform Infrared Spectroscopy Studies

Since the diffraction techniques are not advantageous position in amorphous materials due to the absence of long-range order, the elucidation of the information on the structural elements and symmetry in amorphous materials is a result of the experiments involving the transmission, reflection, refraction and scattering of light in the range of 400-4000cm$^{-1}$. Raman and infrared spectroscopy techniques are the direct probes for such studies. The vibrational spectra provide essential information about the structural arrangement of the glassy network, such as the degree of polymerization of the network forming polyhedra. FTIR transmittance spectra for the samples in the wave number region 1600-4000cm$^{-1}$ were recorded with a resolution of 8 cm$^{-1}$ and with a data accumulation of 40 cycles using a Shimadzu FTIR-8700 Fourier transform infrared
s spectrophotometer. The measurements were made using spectral grade potassium bromide (KBr) pellets containing 1wt% of powdered glass. Sample and KBr powder were mixed in 1:20 weight ratio and the mixture was ground into a fine powder in a clean agate mortar. The powder was pressed to form transparent thin pellets by using a KBr press and they were used to record the FTIR spectra at room temperature.

![FTIR spectrum of NASICON glass](image)

**Fig 2.3: FTIR spectrum of NASICON glass.**

**Table 2.2: FTIR bands for some of the NASICON type glasses**

<table>
<thead>
<tr>
<th>Sample</th>
<th>FTIR band positions (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₅TiP₃O₁₂</td>
<td>1153, 1055, 750, 635, 565, 471</td>
</tr>
<tr>
<td>Na₅TiP₃O₁₂</td>
<td>1150, 1080, 976, 906, 729, 625, 555, 486, 444</td>
</tr>
<tr>
<td>Ag₅TiP₃O₁₂</td>
<td>1159, 1023, 917, 740, 622, 534.</td>
</tr>
<tr>
<td>Li₄NbP₃O₁₂</td>
<td>1175, 1070, 997, 916, 750, 642, 544, 471</td>
</tr>
<tr>
<td>Na₄NbP₃O₁₂</td>
<td>1200, 1080, 984, 902, 741, 633, 536, 444</td>
</tr>
<tr>
<td>Ag₄NbP₃O₁₂</td>
<td>1162, 1026, 914, 740, 623, 525</td>
</tr>
<tr>
<td>Na₂NbCdP₃O₁₂</td>
<td>1169, 1010, 914, 745, 625, 528</td>
</tr>
<tr>
<td>Na₂NbZnP₃O₁₂</td>
<td>1169, 1022, 918, 745, 624, 536</td>
</tr>
<tr>
<td>Na₂NbCuP₃O₁₂</td>
<td>1180, 1015, 922, 756, 632, 536</td>
</tr>
<tr>
<td>Na₂NbPbP₃O₁₂</td>
<td>1153, 1022, 906, 740, 605, 532</td>
</tr>
<tr>
<td>$Li_{5-x}Nb_xTi_{1-x}P_3O_{12}$ FTIR band position in cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>---</td>
</tr>
<tr>
<td>x=0</td>
<td>1153, 1055, 993, 750, 635, 565, 471</td>
</tr>
<tr>
<td>x=0.25</td>
<td>1155, 1059, 997, 748, 642, 563, 471</td>
</tr>
<tr>
<td>x=0.50</td>
<td>1151, 1059, 999, 759, 642, 563, 465</td>
</tr>
<tr>
<td>x=0.75</td>
<td>1159, 1070, 993, 752, 642, 559, 471</td>
</tr>
<tr>
<td>x=1.0</td>
<td>1175, 1070, 997, 916, 750, 642, 544, 471</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$Na_{5-x}Nb_xTi_{1-x}P_3O_{12}$ FTIR band position in cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>x=0</td>
<td>1150, 1080, 976, 906, 729, 625, 555, 486, 444</td>
</tr>
<tr>
<td>x=0.25</td>
<td>1159, 1082, 976, 903, 727, 624, 550, 471, 434</td>
</tr>
<tr>
<td>x=0.50</td>
<td>1167, 1082, 978, 891, 731, 629, 542, 484, 438</td>
</tr>
<tr>
<td>x=0.75</td>
<td>1176, 1082, 980, 897, 733, 629, 540, 474, 446</td>
</tr>
<tr>
<td>x=1.0</td>
<td>1200, 1080, 984, 902, 741, 633, 536, 444</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$(Li_{1-x}Na_x)<em>4NbP_3O</em>{12}$ FTIR band position in cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>x=0</td>
<td>1175, 1070, 997, 916, 750, 642, 544, 471</td>
</tr>
<tr>
<td>x=0.20</td>
<td>1180, 1076, 987, 918, 748, 628, 552, 481, 451</td>
</tr>
<tr>
<td>x=0.40</td>
<td>1192, 1080, 991, 906, 748, 628, 567, 552, 447</td>
</tr>
<tr>
<td>x=0.60</td>
<td>1192, 1080, 987, 918, 741, 632, 552, 471</td>
</tr>
<tr>
<td>x=0.80</td>
<td>1199, 1080, 984, 903, 741, 633, 536, 447</td>
</tr>
<tr>
<td>x=1.0</td>
<td>1200, 1080, 984, 902, 741, 633, 536, 444</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$(Li_{1-x}Na_x)<em>5TiP_3O</em>{12}$ FTIR band position in cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>x=0</td>
<td>1153, 1055, 750, 635, 565, 471</td>
</tr>
<tr>
<td>x=0.20</td>
<td>1130, 1049, 976, 926, 744, 629, 571, 463, 432</td>
</tr>
<tr>
<td>x=0.40</td>
<td>1138, 1053, 984, 922, 741, 632, 567, 474, 444</td>
</tr>
<tr>
<td>x=0.60</td>
<td>1145, 1050, 972, 918, 736, 628, 571, 478,</td>
</tr>
<tr>
<td>x=0.80</td>
<td>1149, 1084, 972, 914, 733, 626, 555, 450</td>
</tr>
<tr>
<td>x=1.0</td>
<td>1150, 1080, 976, 906, 729, 625, 555, 486, 444</td>
</tr>
</tbody>
</table>
The FTIR spectra of two different glasses are shown in Fig. 2.3. These bands are assigned to the various vibrational contributions of the basic phosphates. The spectra endorse that the sample are fully vitrified as there are no traces of initial precursors (absence of carbonate IR peaks in the region 1500-1400cm\(^{-1}\)). Table 2.2 lists the assignments of FTIR bands based on the standard literature references [18-23]. The origin of the bands at lower wave numbers, namely, below 600cm\(^{-1}\), is not quite clear. It is usually assumed that in this range bands originate from vibrations of large groups of atoms, like 3,4-member rings or short chains. The continuous spectrum observed in the region between 1200cm\(^{-1}\) to 890cm\(^{-1}\) assign to the symmetric and asymmetric stretching modes. In this region the superposing of band vibrations of structural forms, mentioned above, as well as the bending vibrations of P-O-P. The peak at ~540cm\(^{-1}\) and the weak shoulder peak at ~640cm\(^{-1}\) together constitute a band. The position of this band corresponds to the asymmetric bending modes of the PO\(_4\) ion in the spectra [24]. An absorption band present in this region 500–650cm\(^{-1}\) in all glasses is attributable to O–P–O bending modes [24, 25]. The weak band at ~460cm\(^{-1}\) is also assigned to bending mode of the PO\(_4\) tetrahedra [24-26]. Superposing of bands due to vibrations of structural forms,
mentioned above, as well as the bending vibrations of P–O–P and P–O–Nb bridges give continuous spectrum usually observed in this region [23]. The vibration band at 1175 cm\(^{-1}\) is due to the P\(_2\)O\(_7\)^4 pyrophosphate contribution present in the glass [16, 27]. In Ti containing glass the band 750 cm\(^{-1}\) is assigned to [TiO\(_6\)] entities. Particularly strong vibration bands at 565 cm\(^{-1}\) can be taken as indication of octahedrally coordinated Ti [27]. In niobium containing glasses the bands of P-O-P and O-Nb-O are similar [27]. The strong vibration peak present at \(~900\) cm\(^{-1}\) may be due to the contribution of [NbO\(_6\)] vibrations [29].

2.3 Electrical properties

When an external electric field is applied to any material medium, a finite amount of charge transport by either electrons or ions takes place resulting in a direct current, \(I_o\) and polarization displacement current, \(I_p\). The magnitudes of \(I_o\) and \(I_p\) may vary in wide limits according to the nature of the material medium. The materials medium is said to be insulator if the magnitude of \(I_o\) is found to be very small in comparison to \(I_p\) and in such materials the phenomena of polarization and relaxation dominate. If \(I_o\) dominates, the medium is said to be a conductor of electricity. Basically when a dielectric material is subjected to an electric field the polarization takes place due to induced dipole moment or due to rotation of permanent electric dipoles present in the materials. In dielectric materials, the possible polarizations are the electronic, ionic and orientation polarization. In this mechanism the charges are locally bound in atoms, in molecules or in the structure of solids. Electronic polarization occurs due to the shift in the electronic charge cloud of the atom with respect to the positive nucleus, which induces dipole moment under the influence of local electric field. In ionic polarization, the net induced dipole moment is due to the displacement of positive and negative ions from the net equilibrium position. In orientation polarization, the orientation of molecular dipoles contributes to the total polarizability. Some mobile charges either electrons or ions can also be found in dielectrics and may move by hopping between localized sites. If the hopping is continued only to limited paths it does not produce dc conduction which requires transfer of charge from one electrode to the other. The macroscopic behavior of a dielectric can be understood by considering the dielectric in between a parallel plate capacitor.
2.3.1. Impedance spectroscopy

Generally the electrical conductivity and relaxation process in fast ion conducting glasses play an important role and these are often the deciding factors about the suitability of the material for a particular solid state ionic device. Therefore, the extraction of true or intrinsic nature of ion conduction mechanism is essential for a material. Impedance spectroscopy is a powerful method for electrical characterization of various ion conducting solids. It is capable of determining the contributions of individual ion conductivity and or electrode process [30, 31]. Electrical response of a system can be determined by several single processes in solid state ion conductors. The vital property of impedance spectroscopy is its exclusive capability to distinguish the different steps in an ion conducting process including the detailed information about the surface and bulk properties. In contrast to dc measurements, frequency dependent complex impedance measurements generally give more detailed information on the electrical properties of a system. Impedance measurements are performed by applying small sinusoidal potential or current to the sample and measuring its current or potential response over a wide range of frequencies. Individual resistive processes can usually be distinguished via varying the frequencies by several orders of magnitude. In 1969, Bauerle was the first researcher applied the technique for ion conducting materials to differentiate between the bulk, grain boundary and electrode resistances [32]. Since then impedance spectroscopy become the most powerful tool to investigate a wide range of ionic conductors such as polymers, ceramics and glasses.

The graphical representation are commonly applied for the complex function, $Z$, in order to analyze the impedance measurements is the Nyquist plot, where the real and imaginary parts of impedance are plotted on linear axis against one another in one plane as shown in the Fig. 2.4. The lower frequency data are represented on higher values of impedance in x axis of the Nyquist plot. This representation is widely used for the interpretation of the ion conducting materials. According to the impedance spectra an electrical network representation called equivalent circuit can be constructed which interprets various contributions to the electrical circuit. Optimization of impedance analysis via equivalent circuit simulation has the basis to regard the measured impedances as network impedance elements[33, 34]. This network model has to
approximate the measured impedance well over the whole frequency range and it can consist of resistors (R), capacitors (C), inductors (L), Warburg impedance (W) and constant phase element (CPE). Each of these elements can be characterized in Nyquist as well as in Bode plots. Serial or parallel combinations of these elements produce the impedance plots. When modeling an ionic process, an ideal capacitor assumes that the surface under investigation is homogeneous. Irregular electrode surface, which is usually due to surface roughness or non-uniformly distributed properties, leads to a dispersion of the parameters [35].

\[ Z_{\text{CPE}} = \frac{1}{Q (i\omega)^n} \]  

\( (2.5) \)
where $n$ is an empirical constant having values between 0 and 1 [39]. When $n=1$, CPE acts as an ideal capacitor where $Q=C$ and when $n=0$, CPE is treated as an ideal resistance where $Q=R$. The parameter $n$ is a measure for the degree of depression in Nyquist plot. Parallel connection of $R$ and $C$ circuit is a semicircular in Nyquist plot. It is perfect semicircle for $n=1$ and depressed semicircle for $n<1$. The semicircle has an intercept on the $Z'$ axis at low frequency and the $Z''$ has maximum where $\omega RC=1$. The imaginary part of the impedance reaches maximum at a frequency, $\omega_{imp}=1/RC$ and it is time constant $\tau_{imp}=1/\omega_{imp}$ and treated as a hopping charge relaxation time.

When two RC elements are present in the systems, each parallel RC element gives rise to a semicircle in the complex impedance plane. Two well separated semicircles in the complex impedance plane are represented by constructing two serial RC elements as exemplified in Fig. 2.5. For example, in real polycrystalline systems two semicircles can be observed due to bulk and grain boundary phenomena. This could be encountered when there is a difference in magnitude as shown in Table 2.3 for the capacitances of the observed processes. Therefore, the capacitance can be calculated for each process and its magnitude gives strong information on the physical origin of the semicircles.

**Table 2.3: Typical order of magnitude of some common capacitance.**

<table>
<thead>
<tr>
<th>Capacitance [F]</th>
<th>Responsible Phenomenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-12}$</td>
<td>Bulk</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>Minor, second phase</td>
</tr>
<tr>
<td>$10^{-11}$-$10^{-8}$</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>$10^{-7}$-$10^{-5}$</td>
<td>Sample-electrode interface</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>Electrochemical reaction</td>
</tr>
</tbody>
</table>
2.3.2. AC response and conductivity

The conductivity process is visualized as a series of consecutive and independent hops of ions over the barriers along the direction of an electric field. The measurement of conductivity is perhaps the most widespread application of impedance spectroscopy and numerous examples can be found in which the conductivity is indeed essentially independent of frequency over many decades. However, there are also examples in which, even after correct treatment of experimental data, considerable dispersion of the conductivity remains. In many non-metallic ionic conductors dc or ac electrical conductivity is the result of diffusion of ions through the conductors. The process of ions through fast ionic conductors, enter into a wide range of other phenomena of concern to solid state physics, chemistry, metallurgy and material science. The diffusion of ions which follows on the existence of gradients in chemical or isotropic composition *i.e.*, solid state diffusion is basic to these interests. The electrical conductivity of ionic material, particularly in the amorphous state, has been much studied in the past few
decades. Hopping conductivity is no longer expected to be independent of frequency in the presence of many-body (long-range) interactions. Following the work of Jonscher [38, 40], who showed that a large number of dive, the presence of interactions has been invoked by Almond et al., [41-43] to explain the observation of frequency dispersion in the conductivity of a number of solid electrolytes. These authors expressed the ionic conductivity of a number of materials by the following expression:

\[ \sigma'(\omega) = \sigma_{dc} + A\omega^n \]  

(2.6)

where \( \sigma_{dc} \) and A are the scales of dc and ac conductivities, respectively, and \( n \) is related to the nature of physical process controlling the conduction of ions and the second term is of the CPE type. Using Jonscher's empirical equation, this expression was rewritten in the form:

\[ \sigma'(\omega) = K\omega_p^p + K\omega_p^{1-n} \omega^n \]  

(2.7)

where \( K \) is the dc pre-exponent, which depends on the concentration of carriers, and \( \omega_p \) is the hopping frequency of the ions. Combining these two equations allows the calculation of the hopping rate:

\[ \omega_p = (\sigma_{dc}/A)^{1/n}. \]  

(2.8)

The high temperature limiting vale of \( \omega_p \) is equal to the attempt frequency, which is independently accessible by infrared measurements. With this \( \omega_p \), it is possible to estimate the carrier concentrations. According to Jonscher, the source of power-law behavior in hopping conductors is relaxation of the ionic atmosphere after the movement of a particle. A quantitative model based on a similar idea has been developed by Funke [44]. It is assumed that immediately after an ion hops to a new site (new minimum in lattice potential energy), it is still displaced from the true minimum in potential energy, which includes contributions from other mobile defects. At longer times the ion may either hop back to its initial site or the other defects will relax so as to move the true minimum closer to, and eventually coincident with, the new lattice site. The dynamics of this model have been developed, and apparently they predict upper and lower frequency-limiting conductivities and, in between, a region of power law dependency of the type expressed by the CPE. Unlike simple CPE response, the complex plane arcs approach the real axes vertically, corresponding to upper and lower limits to the relaxation time of the system. Depending on the frequency of the measurement, the processes of diffusion of
ions with different jump probabilities will contribute different amounts to the total conductivity. At a frequency corresponding to each transition rate, a new conductivity process with higher activation energy will begin to contribute to the total. It is evident that the overlap of several different processes will lead to dispersion over a wide frequency range.

An alternate approach of complex electric modulus formalism was adopted in the field solid state ionics because it discriminated against electrode polarization and other interfacial effects. That is the impedance and conductivity formalism might emphasize inter-granular conduction process whilst the electric modulus would be dominated by bulk effects. This has been introduced by Macedo et al. called electric modulus, \( M^* = 1/\varepsilon^* \), where \( \varepsilon^* \) is the complex permittivity, which tend to emphasize bulk properties at the expense of interfacial polarization [45,46]. Typical features of \( M^*(\omega) \) include a broad, asymmetric peak in the imaginary part and a sigmoidal step in the real part. Proponents of the modulus approach interpret the broad, asymmetric Gaussian-like shape of \( M^*(\omega) \) as indicative of a non-exponential decay of the electric field in response to an applied displacement field [45, 47]. This decay is reasonably well described by a stretched exponential defined by Kohlrausch William-Watts forms [48, 49] as:

\[
\phi(t) = \exp \left[ - (t/\tau)^\beta \right], \tag{2.9}
\]

which is related to \( M^*(\omega) \) as:

\[
M^*(\omega) = \frac{1}{\varepsilon^*} \left\{ 1 - L \left( -\frac{d\phi}{dt} \right) \right\} \tag{2.10}
\]

where \( L(x) \) is the Laplace transform of x the stretching parameter \( \beta \) is approximately equal to \( 1/W \), where \( W \) is the full width at half maximum (FWHM) of \( M''(\omega) \) normalized to that of Debye process. The smallness of the exponent \( \beta \) characterizes the degree of non-Debye behavior. This particular decay function is also used to describe dipolar reorientation in super cooled liquids [50, 51] and is found in a variety of other relaxation phenomena in amorphous materials including mechanical, volumetric, nuclear magnetic resonance, and magnetic relaxation. The shapes of the Williams-Watts derived \( M'' \) plots lie between the symmetric plots expected from log-normal and Cole-Cole forms and the highly asymmetric Cole-Davidson form. Here the parameter \( \beta \) was found to be largely independent of temperature.
2.3.3. Electrical measurements

The electrical measurements were performed with impedance analyzer (Alpha-A 4.2 Analyzer, Novo Control, Hundsangen, Germany) which was combined with the ZG 4 impedance interface in a two probe method. This system is comprised of the Novocontrol alpha dielectric analyser, the automated liquid nitrogen (LN₂) quatro temperature control system, and the two-wire ZGS active sample cell. Silver paste was applied on opposite faces of the pellets as electrodes. Measurements and data recording were performed with WinDeta data analysis program by the central computer assisted controlling of all components. The equipment was designed to measure very high impedance values over a wide range of frequencies varying from 0.01Hz to 10MHz. The set up for impedance spectroscopy cell is schematically shown in Fig. 2.6. For some of the samples both faces of the samples were polished by using silicon carbide sheet and silicon carbide powder (mesh size 800) with water as free lubricant. Then the glass samples were washed with flowing water so that no impurity left in the surface. The washed samples were slowly heated up to 423 K and were held at this temperature for 1 h to remove the water from the surfaces. Silver paint was pasted on parallel faces of the polished sample, and the sample was fixed in a spring loaded sample holder.

Fig. 2.6: Schematic representation of the set up for impedance measurements.
The polished glass samples whose diameters were 1cm and thickness in the range of 0.9mm to 1.2mm were squeezed between the electrodes are mounted over two outer platinum electrodes, which established the connection to the impedance analyzer through the platinum wires. The electrodes were made tight enough with the help of a steel spring load in order to keep the sample in contact with the electrodes. The cell was then covered with a stainless steel which is connected to the liquid nitrogen cell in order to allow the measurements to be performed under inert conditions. The temperature of the cells is attained by heating the N\(_2\) gas and the cell does not have the contact with the outer atmosphere since vacuum is produced between the cell and the atmosphere. The measurements were performed with variation of 10K with the error of ±0.1K min\(^{-1}\).

For the some of the samples the electrical measurements were performed by placing the cell in a horizontal tube furnace and the temperature was controlled by a thermocouple in close vicinity of the sample. Parallel conductance and capacitance were measured using a Hioki 3532-50 LCR Hitester in the frequency range 100 Hz to 1 MHz for various temperatures [52, 53]. Before starting the electrical conductivity measurements, the samples were heated at 393K in the sample holder for stabilization of the electrodes. The real part, \(Z'(\omega)\) and imaginary part, \(Z''(\omega)\) of complex impedance, real part of ac conductivity \(\sigma'(\omega)\), real part, \(M'(\omega)\) and imaginary part, \(M''(\omega)\) of electric modulus are calculated using:

\[
Z'(\omega) = \frac{G}{G^2 + \omega^2 C^2}
\]

\[
Z''(\omega) = \frac{C\omega}{G^2 + \omega^2 C^2}
\]

\[
\sigma'(\omega) = \frac{Gd}{A}
\]

\[
M'(\omega) = \frac{\omega\varepsilon_0 AD Z''}{d}
\]

\[
M''(\omega) = \frac{\omega\varepsilon_0 AD Z'}{d}
\]

where \(G\) and \(C\) are the measured parallel conductance and capacitance and \(\omega=2\pi f\), \(f\) being the frequency in Hz, \(A\) is the electrode area, \(d\) is the thickness of the sample, \(\varepsilon_0=8.856\times10^{-14}\text{F/cm}\) is the permittivity of the free space. The experimental results derived
from different formalism are interpreted using the theories of hopping conduction in addition to the microscopic features of glasses in the forthcoming chapters.
References