CHAPTER 3- Experimental Details

In this chapter, details on sample preparation and characterization techniques are given.

3.1 Introduction

The present chapter includes a discussion on various techniques and methods used for preparation, synthesis, characterization and transport properties of lithium ion conducting ceramic solid electrolyte systems.

3.2 Sample preparation method used in the present study

The method adopted to prepare ceramic (poly) crystalline samples is described below:

Laboratory grade reagents were procured from the vendors. These reagents were certified 99.99% pure. The reagents were treated in a dry atmosphere to avoid contamination due to moisture. All the reagents were in form of fine white powder. Based upon mole fraction proportion and their molecular weight in the chemical formula, different ingredient chemicals were weighed using a digital weighing balance. The accuracy of the instrument was up to 0.01 milligram. Hand contact was avoided by using gloves while weighing the samples. 4 samples were prepared in each series. These samples were of 4 different concentrations. The mole fraction and hence the amount of chemicals in each sample of a series was different.

The general formula of the samples of each series is given below: $Li_{1.3}Al_xM_{0.3-x}Ti_{1.7}(PO_4)_3$ (where M = Y, Ga and Sc). However the basic structure of the above mentioned system is $LiTi_2(PO_4)_3$ (LTP) which is a rhombohedral $R\bar{3}c$ structure [1-5]. The above mentioned trivalent cations were chosen to replace the Al^{3+} in the above system and thereby study the electrical properties of the solid ionic material which is a polycrystalline ceramic by nature.

The series are given below according to the replacing cation species and the amount of doping done in each of the series.

a) $Li_{1.3}Al_xY_{0.3-x}Ti_{1.7}(PO_4)_3$ (x = 0.01, 0.03, 0.05, 0.07, 0.10 and 0.15)

$Li_{1.3}Al_xY_{0.3-x}Ti_{1.7}(PO_4)_3$ (x = 0.01 and 0.15) – heat treatment for 2 and 3 hr

b) $Li_{1.3}Al_xGa_{0.3-x}Ti_{1.7}(PO_4)_3$ (x = 0.01, 0.03, 0.05 and 0.07)

c) $Li_{1.3}Al_xSc_{0.3-x}Ti_{1.7}(PO_4)_3$ (x = 0.01, 0.03, 0.05 and 0.07)

Following methodology was adapted to synthesise ceramic samples.

Laboratory grade Lithium carbonate (Li_2CO_3), Ammonium dihydrogen phosphate (NH_4H_2 (PO_4)), Yttrium oxide (Y_2O_3), Gallium oxide (Ga_2O_3), Scandium Oxide (Sc_2O_3), Titanium oxide (TiO_2), Alumina (Al_2O_3) (LobaChemie, Mumbai, India) were taken according to their weight percentages in a cool and dry atmosphere. These powders were weighed according to their weight percentage contribution for the solid state reaction. They were mixed and ground using agate mortar and pastel for 30 min. This mixture was heated in ceramic ampoules in an electrical furnace upto 873 K for 20 minutes. Due to this water vapour (H_2O) and carbon dioxide (CO_2) were released from the compounds. Later, it was allowed to slowly cool in the furnace itself. On cooling, the compounds were again ground in an agate mortar pestle for 15-20 minutes and heated to 1073 K for 45 minutes. It was left in furnace for cooling slowly. The last cycle of hand grinding was done for 30 minutes resulting in a very fine white powder. Pellets of 2-3 mm thickness and approximately 10 mm diameter were prepared using a die set on a hydraulic pelletizer at a pressure of 5 Tons psi. The pellets were heated up to 1173 K for 1hr and left in furnace to slowly cool. The resulting pellets were bright white with a smooth surface. All the above mentioned treatment – hand grinding, mixing, pelletizing etc was carried out at standard temperature of 19-20° C at a humidity of less than 10-15% water vapour content.

Pellets of $LiTi_2(PO_4)_3$ (LTP) and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) samples in same batch and by same procedure for comparison and reference. LTP and LATP samples were also characterized the same way as samples in other series, for their electrical and structural properties. The general formula of the above systems are based on $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) system. The LATP NASICON compound is known to have maximum Li^+ ionic conductivity. The optimum Li^+ conductivity is obtained for the above concentration: $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ that is, for $x = 0.3$. Hence it is important to characterize and study the LATP system as well.

Two samples of concentration of $x = 0.01$ and 0.15 were subjected to further heat treatment at 1273 K for 2 hrs. and 3 hrs duration and left in the furnace for slow cooling.

3.3 X-ray Diffraction (XRD) studies

The X-ray Diffraction studies were carried out using the Rigaku MiniFlex Cu Kα line (λ=1.5405 Å). The samples were stored in a cool and moisture free area before performing the XRD measurements. The XRD was performed in a vertical geometry. The below figure depicts the X-ray Diffractor Machine (Rigaku Miniflex bench top 600 model). The assemblies of electron gun which generates high energy electron beam to strike Copper metal anode and produce Cu Kα x-rays, collimator slits, a charge coupled device (CCD) detector etc, are housed in the benchtop chamber. The chamber was maintained at a vacuum pressure of 10^{-3} Torr. The CCD detector consists of grids of small semiconductor detectors interfaced with sensors. An variation in the reception from the samples was faithfully measured by the CCD detector produced pulses proportional to the intensity of diffracted x-rays. X-ray diffractometers are designed in Bragg- Brentano geometry. This is depicted in Fig. 3. below.

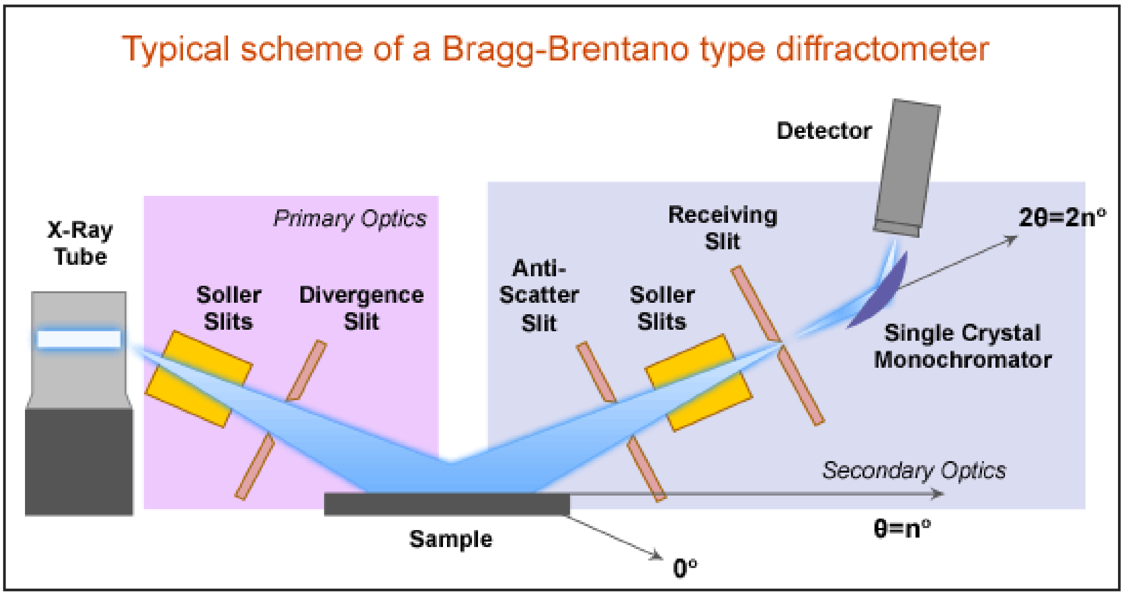

Fig. 3.1 Schematic view of working of X-ray diffractometer.

Step scan method with a step size of 0.2° was used to collect the diffracted x-rays. In this method of collection, the detector is adjusted stationary at a radial angle and distance from the sample. The sample holder is rotated in small steps by a goniometer while the sample is continuously exposed to a steady beam of x-rays. Great care is taken to ensure a steady voltage at the electron gun and maintain a steady flow of x-rays. Even before the x-rays are generated, current is passed through the voltage regulator to ensure a steady voltage at the source. This ensured a very steady and stable flux of x-rays which are collimated by (Söller) slits. The generator settings in our case were put at 40 mA and 45 kV. The collimator slits are specially designed with extreme (micrometer range) precision for variables like aperture position, blade motion etc and their function and performance varies with respect to air, high vacuum (HV) and ultra high vacuum (UHV). A separate assembly of cooling system (pumps, pipes, and circuits) for the generator and anode were interfaced with the XRD machine. The entire XRD facility was housed in a air conditioned room which ensured cool and dry atmosphere necessary for the XRD system to function.

Initially the prepared powder of the ceramic was filled in the sample holder and mounted in a horizontal plane. XRD beam was scanned in the range of 10º to 70º. The powder diffraction was performed for LAYTP series (normal and heat treated). The samples in form of pellets were used for XRD patterns of LAGTP and LASTP series. These samples were mounted in horizontal plane and X-ray beam was scanned in the same range of 10º and 70º. The XRD scan was recorded in continuous scan mode for a slit width of 0.8709° and step size of 0.008°. Before the samples were mounted in the XRD scan, the samples were dried using a hand dryer to remove any traces of moisture.

Later, all samples of LAGTP, LASTP and LAYTP series were performed in their pellet form only. The pellets were dried and stored in a moisture free area before and during the XRD scan. For XRD patterns of pellet samples, continuous scan method was used to collect the diffracted x-rays. According to this method, the sample is exposed to a steady flux of x-rays and detector is rotated in a circular plane around the sample for the pre-set values of 2θ degrees (between 10° and 70°) with a step size of 0.2°. The pulses of energy were recorded by the CCD detectors for different diffraction angles. This ensured all x-rays were collected. The size of collimator slit was set at 0.8709°. The goniometer radius was 240 mm. All the values of the above mentioned parameters were filled using an interfacing computer. The motion of CCD detectors, the goniometer, the voltages for generator, vacuum pump, the cooling system etc were computer controlled.

The files were saved in the interfaced computer with extension .XRDML. The software calculated the height (peak intensity), area under the peaks , FWHM for the peaks and the d-spacing corresponding to peaks at different 2θ values.

Fig. 3.2 A typical Rigaku Miniflex bench top model X-ray Diffractometer

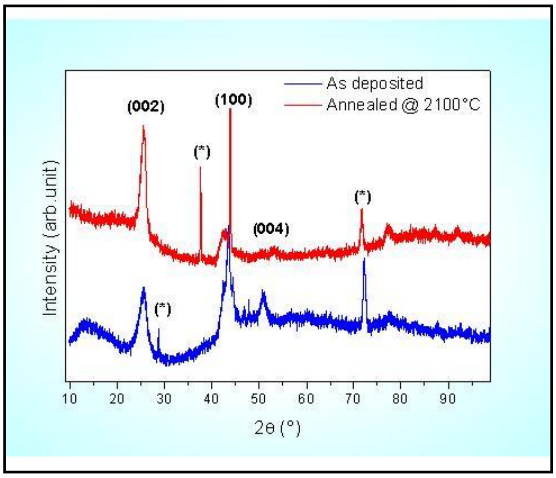

Fig. 3.3 A typical XRD pattern indicating peaks corresponding to different compounds

Fig. 3.2 shows a typical Rigaku Miniflex model of x-ray diffractometer with Bragg-Brantano geometry while, Fig. 3.3 shows a typical XRD spectra which is a plot of intensity versus angle of diffraction (θ).

3.4 Density Measurements

In the present study, Archimedes method was used to measure the density of the samples. According to this method, the mass of sample in air and in the displacing liquid have to measured very accurately. To measure the weight of sample in air and then in a liquid (methanol) a very sensitive digital weighing balance (micro balance) of ***A&D*** Japan Model ADGR 202 was used. It had an accuracy of 0.01 mg in measurement. For density measurements, special density kit for this electronic balance has been used.

Fig.3.4 (below) depicts a micro balance and fig. 3.5 shows a typical assembly of the lower pan along with the sample, immersed in the methanol.

The samples were weighed in cool and moisture free atmosphere. Methanol was chosen since it does not react with the sample material. All measurements were carried out in a cool atmosphere at 18-20° C. It was also ensured the density measurements were performed in dry atmosphere where humidity level was below 10%.

Fig. 3.4 A picture of digital weighing balance

Fig. 3.5 Assembly of weighing pan immersed in methanol

First the weighing pan from the balance was removed and the density pan stand was set on balance. After that the beaker was set on a stand so that it does not touch the density pan stand. The spacers under the beaker stand legs were adjusted such that the legs fit into the grooves of the spacers. Methanol was poured in the beaker. The beaker was placed on the beaker stand. Lastly, the pan was immersed in the methanol. The sample was immersed upto about 10 mm below the surface of the liquid. The RE-ZERO key is pressed to reset the displayed value to zero. First the sample was placed in the upper pan and its weight in air $\boldsymbol{W_{air}}$ was noted. Later, the sample was placed in the lower pan in the methanol, the digital scale was again reset to zero using the RE-ZERO key and weight of sample in methanol $\boldsymbol{W_{methanol}}$ was measured.

3.5 Scanning Electron Microscopy (SEM)

The surface morphology of the prepared ceramic pellet samples was studied by using a computer-controlled Scanning Electron Microscope (JEOL JSM-6380LV) (Fig. 3.6) at 20 kV with 100 µm resolution and 1000 magnification. A typical SEM picture is shown in fig.

3.7. The ceramic pellets were uniformly polished for 2-3 minutes on an emery paper and cleaned using cotton gauze before mounting them on the sample holder in the chamber. This step ensured a cleaner surface for the SEM measurements.

Fig. 3.6 Experimental setup of Scanning Electron Microscope interfaced with computer

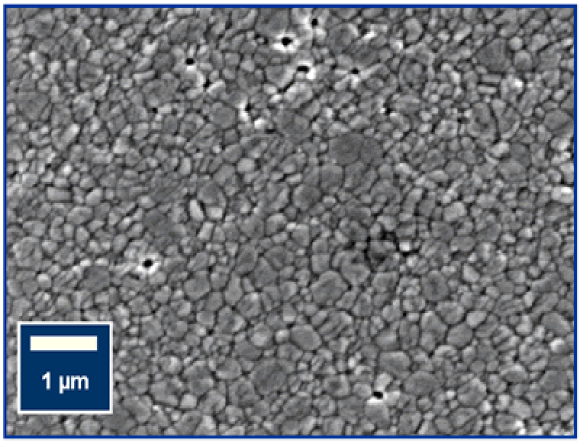

Fig. 3.7 A typical SEM image of grains in a ceramic solid showing with scale (size) indicator

The ceramic pellets were mounted on circular aluminum stubs with double side sticky tapes. The surface of the samples pellets were polished using an emery paper before mounting. The aluminium mounting was transferred in to a chamber. The chamber was evacuated and maintained at a pressure of 10^{-4} Torr using an Edwards Boch vacuum pump. High voltage (upto 15 kV) was applied on the electron gun and smaller voltage (in the range of 1 KV to 4 KV) on the electron lenses to direct the electron beam correctly on the pellet samples and obtain correct contrast in the electron micrograph images. To differentiate amongst the samples on the mounting plate, they were marked by numbers 1, 2, 3 and 4. Other arrangements like automatic brightness and contrast in the image was performed before taking the final images. Images were first contrasted and adjusted for brightness before grabbing (finally saving) them. Care was taken to grab SEM images for different regions on the surface of the pellets. These regions corresponded to grains and grain contacts (boundaries), any special structures like pores, aggregates and peculiar structures near grain boundaries. The SEM micrographs were taken in micrometer range which was roughly to a magnification of 4000X. Some images for LAYTP series were taken up to 7000X. Generally for any sample, initial image at 500X, 1000X, 2000X, 3000X and 4000X was taken. If the image blurred out after this magnification, the image grabbing was stopped after that magnification.

Scanning Electron Microscopy (SEM) (JEOL Oxford Instruments) was performed on the samples to ascertain the microstructure of the prepared samples. The facility was available at The Dept. of Material Science and Metallurgical Engineering, at the M.S.University of Baroda.

3.6 Transference Number Measurement (TN):

The transport number studies were performed to estimate the number of ionic and electronic charge carriers in the solid medium. The transference number measurement was measured using DC polarization method to find the transference number of a solid electrolyte medium for different series. In all the systems, only cations like Li^+ and electrons were presumed to be primary mobile charge carriers. The transference number of charges (cationic) in a superionic system can be defined as the ratio of current due to ionic charges to the total current (due to ions and electrons) in the system. The current due to ionic charges is given as $i_{\mathbf{Li+}}$ and that due to electrons is i_{e-} , then the transference number is given as

$$t_{Li^+} = i_{Li^+} / i_{total} \qquad \text{...............(3.1)}$$

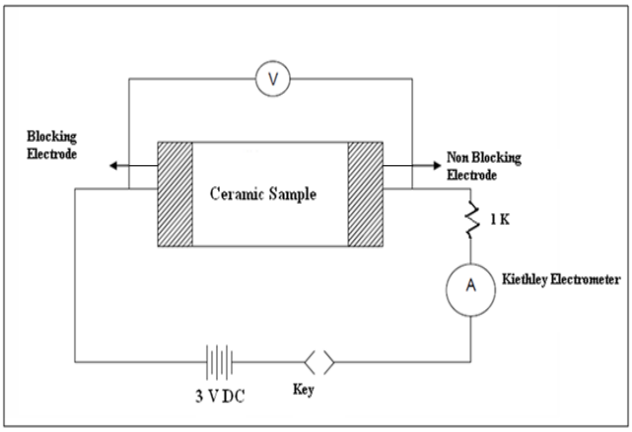

Fig. 3.8 Circuit diagram showing the experimental arrangement for Transport Number measurement

To measure $\boldsymbol{i_{e^-}}$ using the DC polarization method at our lab, a sensitive Electrometer (Keithley model: 6514), a homemade circuit with an on/off switch, a 9 volt battery for DC bias, sample holder, coaxial cables with probes etc were used. The circuit for performing the experiment is shown in Fig. 3.8. The experiment was carried out as follows:

The ceramic pellets were coated with conducting silver paint and sandwiched between the copper electrodes of a homemade sample holder. The arrangement is as follows: Silver | Sample Pellet | Silver.

The sample was put at a DC bias of 3 V from a battery through the leads of the sample holder. The DC bias was adjusted using a variable resistance on a circuit designed as given below. The Keithley electrometer was connected in series to the sample. A resistance of 1KΩ was connected in series to the electrometer which measures current. Due to DC bias the ions move towards cathode. After some time (2-3 hrs) the sample becomes fully charged (that is most of the Li^+ get accumulated at cathode). On connecting a switch, the battery is allowed to discharge. Electrons surge (in the outer circuit) towards the anode side on account of the potential difference created by accumulated positive ions. This surge of electrons is measured by the electrometer which is connected in a series combination. A maximum in the initial current is observed at initial time $t = 0$. This current represents ionic and electronic currents $\boldsymbol{i_{Li^+}}$ and $\boldsymbol{i_{e^-}}$. The current value falls after initial few moments and saturates at a steady low value after some time. That is, the current has a diminishing value and it rapidly decays to a very low value. After some time when saturation is achieved, a very small (negligible) value of electrons flow in the outer circuit. This is due to flow of only electronic charge in the sample and hence is called the electronic current $\boldsymbol{i_{e^-}}$. Typically a discharging cycle will last 8-9 hrs for a single pellet. The electronic current is due to transit of electrons from cathode to anode in the outer circuit. In the experiment, the i_{e^-} is measured and deducted from unity to obtain i_{Li^+}.

$t_{Li^+} = (1- t_e)\%$ gives the percentage of ionic charge carriers in the system. Typically the ionic current is more than 90% for a superionic sample. Thus a typical plot (fig 3.9) of Current vs. Time for a superionic conductor resembles the following figure.

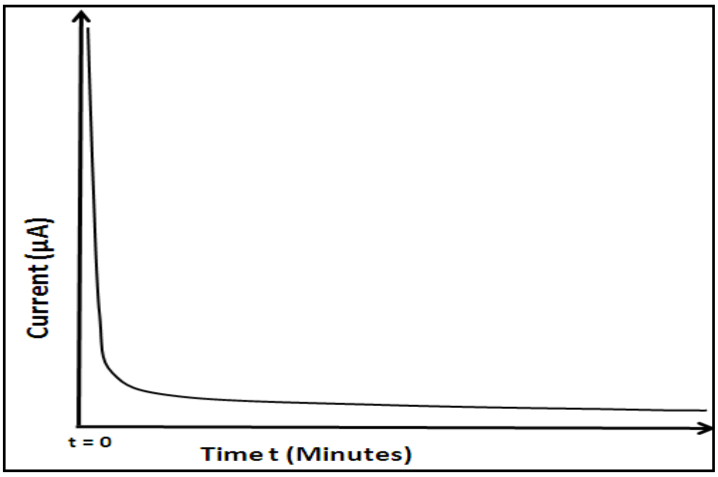

Fig. 3.9 A typical plot of the variation of current with respect to time.

3.7 Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS) is a quantitative technique which probes and estimates the elemental composition on the solid surface of the sample. It gives an idea of atomic % and weight % of the elements that are present on the spot of the surface where the probing is done. It also helps find the percentage composition of any impurity elements and the exact quantities upto which they are present. In our studies, the EDS technique was used to do elemental analysis of samples, since doping of different elements was done for very small concentrations (0.01 to 0.07).

The EDS instrument was interfaced with the Scanning Electron Microscope. Sample mounting and evacuation of the sample chamber were performed in the same step meant for SEM. The samples were mounted in the sample chamber of SEM. This chamber was evacuated to a pressure of 10^{-4} Torr using an Edward Boch rotary pump, before making the measurements. Energy Dispersive Spectroscopy (EDS) measurements were performed using OXFORD EDS analyzer with a Silicon Drift Detector (SDD). The EDS measurements were taken from a point on the surface of the pellet after monitoring in the microscope. Once a smooth and uniform surface was identified using the microscope, EDS measurements were started. Each scan took approximately 2 minutes to record. Images were recorded and saved once the elemental composition was ascertained. Fig. 3.10 below shows the setup of EDS instrument.

Fig. 3.10 Experimental setup of EDS interfaced with SEM instrument and a controlling computer

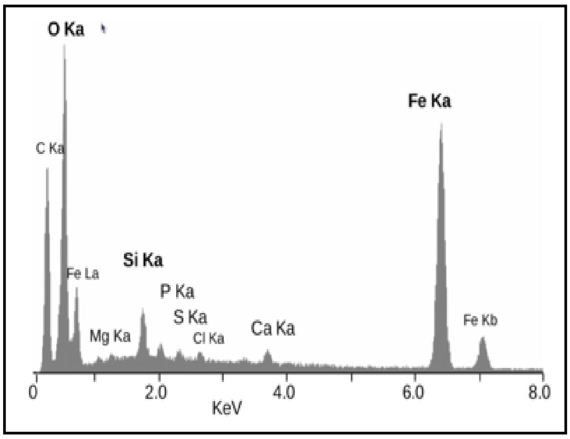

Fig. 3.11 A typical EDS spectrum of elements

A sample chamber is housed with that of the SEM. The first computer controls the Scanning Electron Microscope (SEM) while the second computer controls the EDS. Hence EDS can be performed for the samples for which the SEM has been performed. Experimental arrangement of the EDS (JEOL OXFORD instruments) is shown in the above figure. The arrangement contains vacuum pump assembly below the sample chamber. The computer controlled sample chamber, evacuation system, detector assembly, electron gun and X-ray tube and subsequently cooling system are seen in the figure.

3.8 Impedance Spectroscopy

In this section we have put the all the details about the experimental setup, the measurements etc of the impedance spectroscopy.

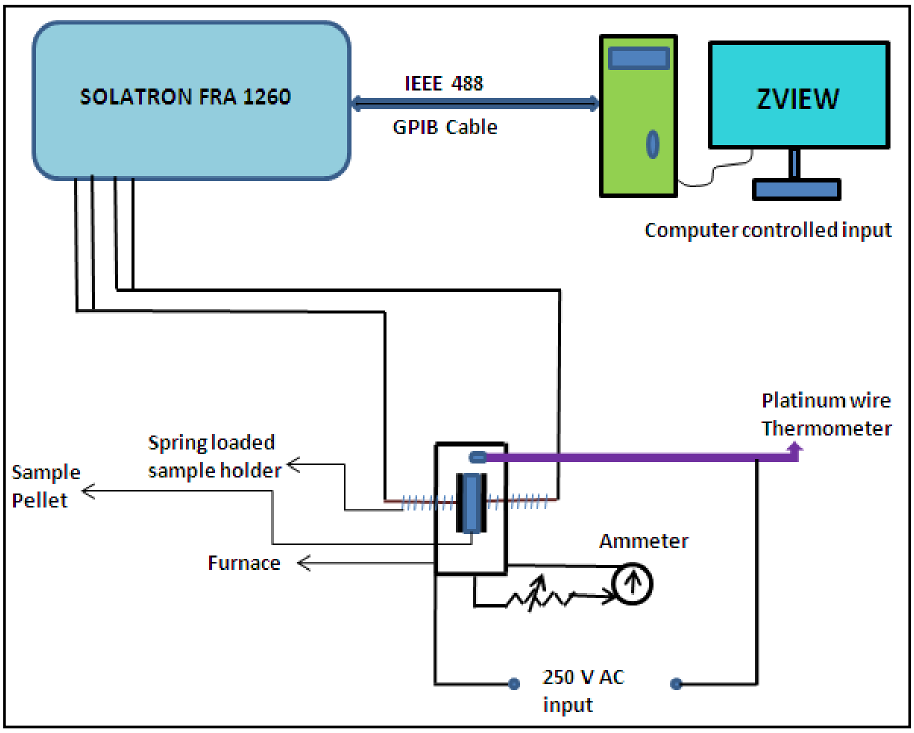

Fig. 3.12 Experimental setup of impedance spectroscopy experiment.

In our case, the complex impedance measurement were carried out using a computer-interfaced impedance analyzer (Impedance Gain/Phase Analyzer, Solartron 1260) in the frequency range of 1Hz to 32MHz at ac signal amplitude of 400 mV at 303-433 K temperatures. Smooth surface of ceramic pellets was obtained by polishing it on both sides with an emery paper. A very thin player of silver paint was applied on the two surfaces of the pellet. Each surface was dried for 15 minutes using an IR lamp. The pellet was then sandwiched between two copper plates of a sample holder. The copper plates had a similar surface area as the pellets. The two surfaces of the copper plates which were in contact with the pellet, were polished and cleaned to remove the oxide layer, at the time of performing the impedance measurements. The sample holder holds the sample using spring loaded copper plates. The springs on both sides apply appropriate tension on the sample. Due to this arrangement the pellet and the copper plate remain in firm contact with each other. The sample holder was connected to the two probes of the impedance analyzer. The analyzer was controlled by a computer interfaced to it. Z-View software was used to set the cell characteristics, the input voltage, the frequency scan and other details. A schematic diagram of the entire experimental setup of the impedance spectroscopy is given in the below Fig.3.12. The data was transferred and stored in the computer via a GPIB cable. The entire assembly consisting of sample and the sample holder was put inside a tubular furnace. The furnace is capable of reaching up to 200° C. A platinum wire thermometer was used as thermostat in the furnace. On setting the thermometer to a given temperature, the relay circuit starts current in the furnace coils. The temperature at which the impedance measurements are to be taken is manually adjusted in the platinum wire thermometer. The relay insures the temperature is fixed and maintained at the desired value until the impedance measurements are carried out. The constantan coils in the furnace are heated due to Joule (heating) effect. Desired value of heat is produced in this way inside the furnace. The sample is heated until the given temperature. The flow of current in the furnace coils stops due to relay action, when the rising mercury in the thermometer comes in contact with the platinum wire. In this way, the sample is heated at increasing temperatures and impedance measurement is carried out. The experimental setup of the SOLARTRON impedance analyser interfaced with a desktop computer, a tubular furnace and a sensitive mercury thermometer is shown in the Figure 3.13.

Fig. 3.13 Experimental setup of Solartron Impedance Analyser interfaced with computer.

The input into the SOLARTRON impedance analyser is obtained in from the two leads. ZVIEW software (ver. 2.6b) is used to collect, chart and extract the data in the computer. We set the frequency interval in which the scan is to be done. Generally a logarithmic scale is adopted in the scan. From the impedance data the conductivity is calculated. The complex impedance spectrum data was used to derive other immitance quantities like ac and dc conductivity, dielectric permittivity and modulus spectra. The data is collected in accumulation mode.

References:

[1] JCPDS Card No. 79-1640

[2] JCPDS Card No. 38-1468

[3] R. Ramaraghavulu, S. Budhhudu, Ceramic International 37 (2011) 3651

[4] K. Arbi, S. Mandal, J.M. Rojo, J Sanz, Chem Mater. 14 (2002) 1091

[5] T. Ishihara, T Akbay, H. Furutani, Y Takita. Solid State Ionics 113-115 (1998) 585

[6] J.W. Evans, C.A Vincent, P.G, Bruce. Polymer. 28 (1987) 2324

******