3.1 Introduction

Amorphous solid electrolytes are a class of solid materials that exhibit some unique physical properties mainly electrical ones. As they are super ion conducting in nature, various tools and methods are employed to understand their chemical, physical, and electrical properties.

This chapter includes a detailed description of the techniques utilized in the present work to achieve the proposed objectives, which include synthesis, characterizations and various studies of prepared glass materials. Three series of glass samples were synthesized using conventional melt quenching technique. Density of these three glassy systems was determined by Archimedes' principle. X-ray powder Diffractometry (XRD) was employed to confirm the glassy nature of prepared samples, while Differential Scanning Calorimetry (DSC) was used to reveal glass transition temperature (Tg). Fourier Transform Infrared (FTIR) spectroscopy was further utilized to characterize the structure of prepared glass samples. Electrical properties of the prepared glass samples were studied by Impedance Spectroscopy technique. Ionic transport number measurements of prepared samples have been carried out using EMF method.

3.2 Preparation of glass samples

Analytical Reagent grade starting chemicals: PbI_2, Ag_2O, V_2O_5 and H_3BO_3 were used to prepare the samples. All the compositions were weighed according to their mole %, crushed and then mixed thoroughly using an agate mortar pestle for 2 hours to ensure proper mixing and homogeneity of the constituents. The glass mixture, kept in a porcelain crucible, was maintained at 400˚C for half an hour to let H_3BO_3 convert into B_2O_3 completely. After that, the samples were melted at 750 to

800˚C (melting temperature varied from series to series) in a muffle furnace for 3 to 4 hours. The melt was poured on a thick metallic copper plate (10 mm thick) and quenched with another similar copper plate kept at room temperature. Thin sheets of dark red brown colored glass samples were obtained. The prepared glass samples were preserved at room temperature in a desiccator to prevent any degradation that might occur due to various environmental factors.

Following three series of glass samples were prepared to study their transport properties;

1. **Series (a):** x PbI_2 - (100-x) [Ag_2O - 2(0.7V_2O_5 – 0.3B_2O_3)]

   where, $5 \leq x \leq 25$ in steps of 5.

2. **Series (b):** y (PbI_2:2Ag_2O) - (100-y) [0.7V_2O_5 - 0.3B_2O_3]

   where, $30 \leq y \leq 55$ in steps of 5.

3. **Series (c):** z (PbI_2:Ag_2O) - (90-z) V_2O_5 - 10B_2O_3

   where, $30 \leq z \leq 50$ in steps of 5.

Here in the first series (a), the effect of variation of iodide salt (PbI_2) on the different physic properties of the host Ag_2O-V_2O_5-B_2O_3 glass has been investigated. In order to see the effect of the salt and the modifier Ag_2O on the glass formers, the fixed ratio of PbI_2 and Ag_2O as 1:2 and it was varied against the mixed formers vanadium pentoxide and borate matrix. Further, in the third glass series (c), the amount of glass former B_2O_3 has been fixed and the other former V_2O_5 has been varied against a fixed ratio of PbI_2 to Ag_2O content to understand the effect of the glass former on the lead silver oxysalt system.

3.3 Experimental techniques

After preparation of the samples, characterization studies were undertaken to understand their basic nature and characteristics.

3.3.1 Density measurements

Density is a primary physical property of any material which exhibits that how closely atoms or molecules are packed in the given material. .

The density of all prepared samples is measured using Archimedes' principle. For this, methanol with a known density ρ_o (= 0.790 g/cm^3) was used as an immersing medium. The bulk glass piece was first weighed in air, and then immersed into the methanol and weighed again using a micro digital balance. From these weighings, density of the given solid specimen can be calculated using the following equation,

$$\rho_{sample} = \rho_{liquid} \times \left(\frac{M_{air}}{M_{air} - M_{liquid}} \right) \qquad \text{……… (3.1)}$$

where, ρ_{sample} = density of the sample

ρ_{liquid} = density of the immersion liquid

M_{air} = mass of the sample in air

M_{liquid} = mass of the sample in liquid

3.3.2 Powder X-Ray Diffraction

X-ray diffraction is a versatile tool to determine the structure of the glass whether it is fully amorphous, crystalline or mixed in nature. One can determine the crystal structure or crystallinity by X-ray powder diffraction which is a popular tool to obtain the information of atomic arrangement in the solids. The parameters such as such as space group, lattice constant, atomic positions, etc., of crystals can be determined by using this technique. In a crystal, since the inter-planar spacing is generally of the order of several angstroms (Å), the atomic planes can diffract electromagnetic waves, like X-rays, whose wavelength is comparable to the inter-planar spacing. A monochromatic X-ray beam will be diffracted if the Bragg condition is satisfied:

$$n\lambda = 2d\sin\theta \qquad \ldots\ldots\ldots \text{(3.2)}$$

where, n is an integer that provides the order of diffraction, λ is the X-ray wavelength, d is the inter-planar spacing, and θ is the glancing angle between the incident beam and the scattering atomic planes.

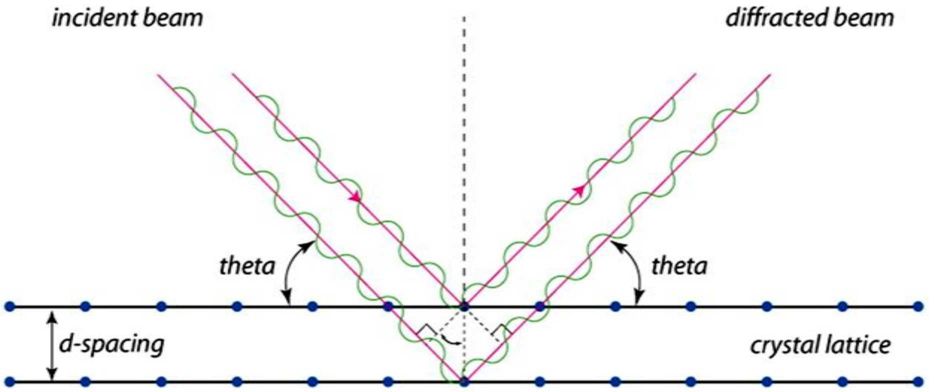

Fig. 3.1. Schematic representation of diffraction of X-rays by a crystal.

Fig. 3.2. Image of the XRD instrument.

In practice, the diffraction angle is commonly specified as 2θ rather than θ. It is well known that in the amorphous materials, *e.g.* glasses and liquids, there is no long-range periodic structure, and hence Bragg's law is inappropriate. Therefore, unlike crystals, amorphous materials do not produce any X-ray or electron diffraction patterns with sharp Bragg peaks.

Instead, characteristic diffused haloes are observed. In the present study, the glassy nature of bulk glasses was characterized by X-ray diffraction analyzer (Shimadzu 6000) Cu-Kα radiation and the data were collected in the 2θ range 10°–80° at a scan rate of 2°/minute at room temperature.

3.3.3 Differential Scanning Calorimetry

Thermal analysis of a material is conducted by observing changes in its physical and chemical properties as a function of temperature and time. Differential Scanning Calorimetry (DSC) is a common technique for determination of melting point of crystals, glass transition (T_g) and Crystallization temperatures of glasses. DSC is used in measuring glass transition temperature, phase changes, purity evaporation, melting, purity crystallization, sublimation, polymerization, heat capacity etc.

In principle, DSC measures the difference in the amount of heat energy (enthalpy) required to keep both sample (encapsulated inside an aluminum pan) and the reference l (an empty aluminum pan or some inert reference encapsulated inside an aluminum pan e.g. Alumina powder) at the same temperature, when both the sample and the reference are heated at a controlled (usually linear) rate.

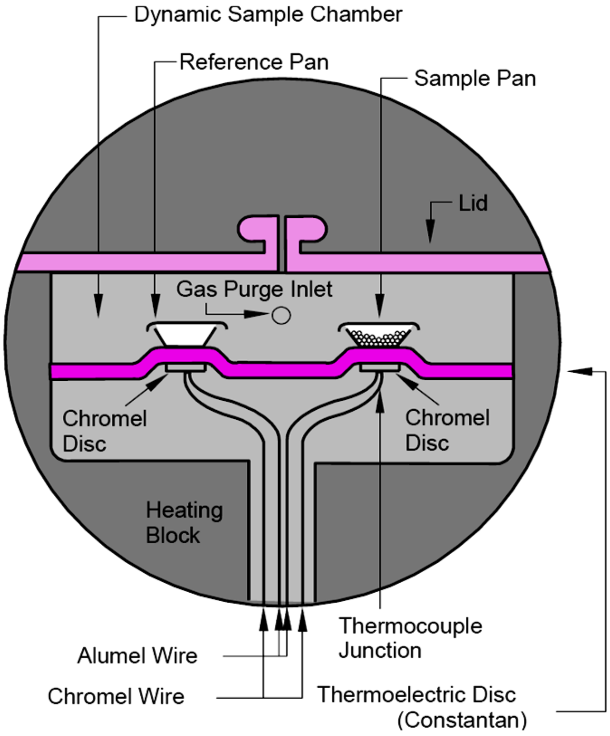

Fig. 3.3. Schematic diagram of a basic heat flux DSC instrument.

Fig. 3.4. Image of the SII *EXStar*-6000 *model* DSC instrument.

In practice, two kinds of DSC instruments are available commercially: (I) Heat-flux design & (II) Power-compensated Design. In the present Investigation, *SII* *nanotechnology EXStar-6000 model* DSC has been utilized, and it is of Heat-flux design.

A heat flux DSC utilizes a single furnace. Heat flow into both sample and reference material via an electrically heated constantan thermoelectric disk and is proportional to the difference in output of the two thermocouple junctions. In this technique, *the difference is calculated between the amount of heat needed to increase the temperature of the sample* and *the heat required to increase the temperature of the reference*. Since DSC is a passive technique, the sensitivity of measurement is very high and the measurements are reliable. The experiment is designed in such a way that the temperature increases linearly. During phase transition, the heat required is either more or less than the reference depending upon the process being endothermic or exothermic in the sample pan. The difference in heat flow between a reference and a sample helps the DSC module to precisely measure the heat released or absorbed during the transition phase. During the experiment, a curve is obtained between the heat flux and temperature or the heat flux and time. Enthalpies of transitions are calculated by this curve. The calorimetric measurement is always carried out in an inert gas atmosphere, e.g. nitrogen gas (N_2) to provide an inert ambient atmosphere as well as to protect the instrument from any contaminations that may occur due to decomposition of the sample at elevated temperatures.

Fig. 3.5 shows a typical DSC curve for a glass specimen on heating process. The first feature appearing in this curve is the glass transition temperature (T_g). The discontinuous change in the specific heat of the glassy sample, which occurs when the glass converts from a solid to a liquid in the glass transformation region, is the indicative of T_g. The glass transition temperature, T_g, is determined by the intersection of the two tangents at the start of DSC endotherm, as shown in Fig.6.

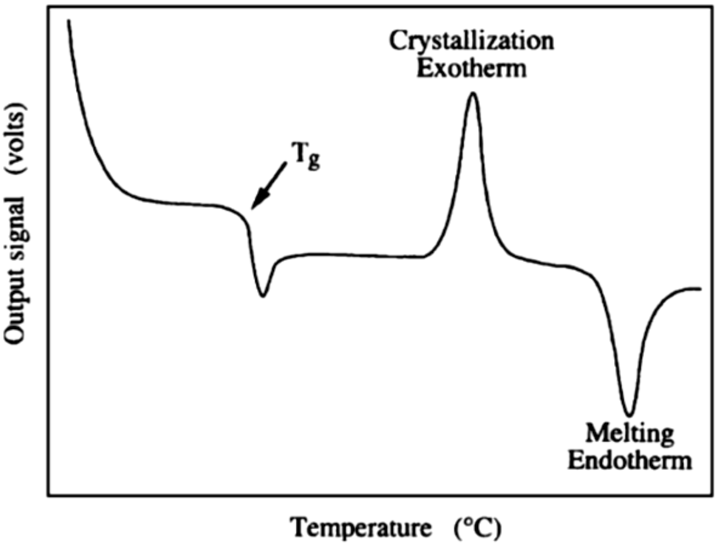

Fig. 3.5. A DSC curve exhibiting a change in specific heat at the glass transformation, an exothermic peak due to crystallization of the glass, and an endotherm due to melting of the crystals formed at the exotherm. (*Reproduced from Ref.* [1])

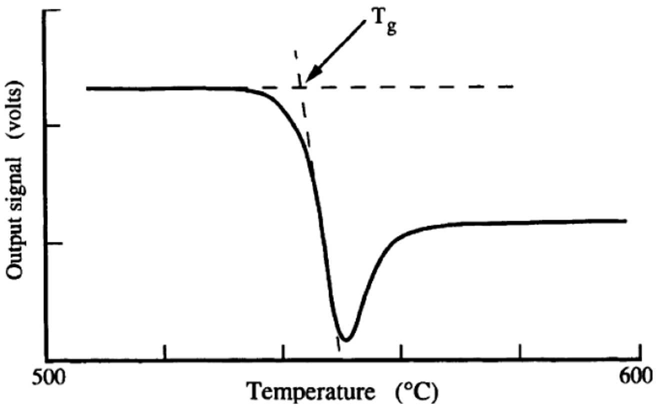

Fig. 3.6. An example of the determination of glass transition temperature, T_g from a DSC curve. (Reproduced from Ref. [1]).

The second feature in the DSC curve (Fig. 3.5) is the exothermic peak due to crystallization of the glass, which involves the evolution of energy [2]. The third feature at the highest temperature in the DSC curve (Fig. 3.5) is the endothermic peak due to melting (the process is accompanied by the absorption of energy) of the crystals. In the present study, the glass transition temperature (T_g) of the investigated glasses was obtained by using a DSC at a heating rate of 10 ˚C/min from room temperature to their melting point under constant flow of N_2 gas.

3.3.4 Fourier Transform - Infrared Spectroscopy

Fourier Transform – Infrared spectroscopy (FT-IR) is a preferred technique of infrared (IR) spectroscopy to identify the molecular compounds and local structures of materials. The IR wavelengths absorbed by the sample are characteristic of its molecular structure. The IR spectra can be presented in either transmission or reflection mode. The molecular vibrations appear as dips in the transmission spectra, and as peaks in the absorption and reflection spectra.

As shown in the Fig. 3.7, an FT-IR Spectrometer employs an interferometer to encode all the wavelengths from the IR source. A detector is used to measure the intensity of transmitted or reflected light at each wavelength. The resulting signal from the detector is then analyzed with a computer using the Fourier transformation to achieve the final FT-IR spectrum for study. The FT-IR spectra are normally portrayed as the percentage of light transmittance or absorbance versus wave number (in cm^{-1}), which is the reciprocal of wavelength.

In the present work, FT-IR spectrometer (Jasco FTIR) in the wave number range of 400-4000 cm^{-1} (*standard resolution* = 4 cm^{-1}) at room temperature was utilized to investigate the structure of Lead Iodide doped Silver-Boro-Vanadate glasses. Dry potassium bromide (KBr) powder (with a quantity of 1-2 mg) and a very small amount of glassy powder ($\mathrm{KBr:sample} = 100{:}1$) were mixed, grinded and then the resultant mixture was compressed to form thin pellets of 0.5 to1 mm thickness.

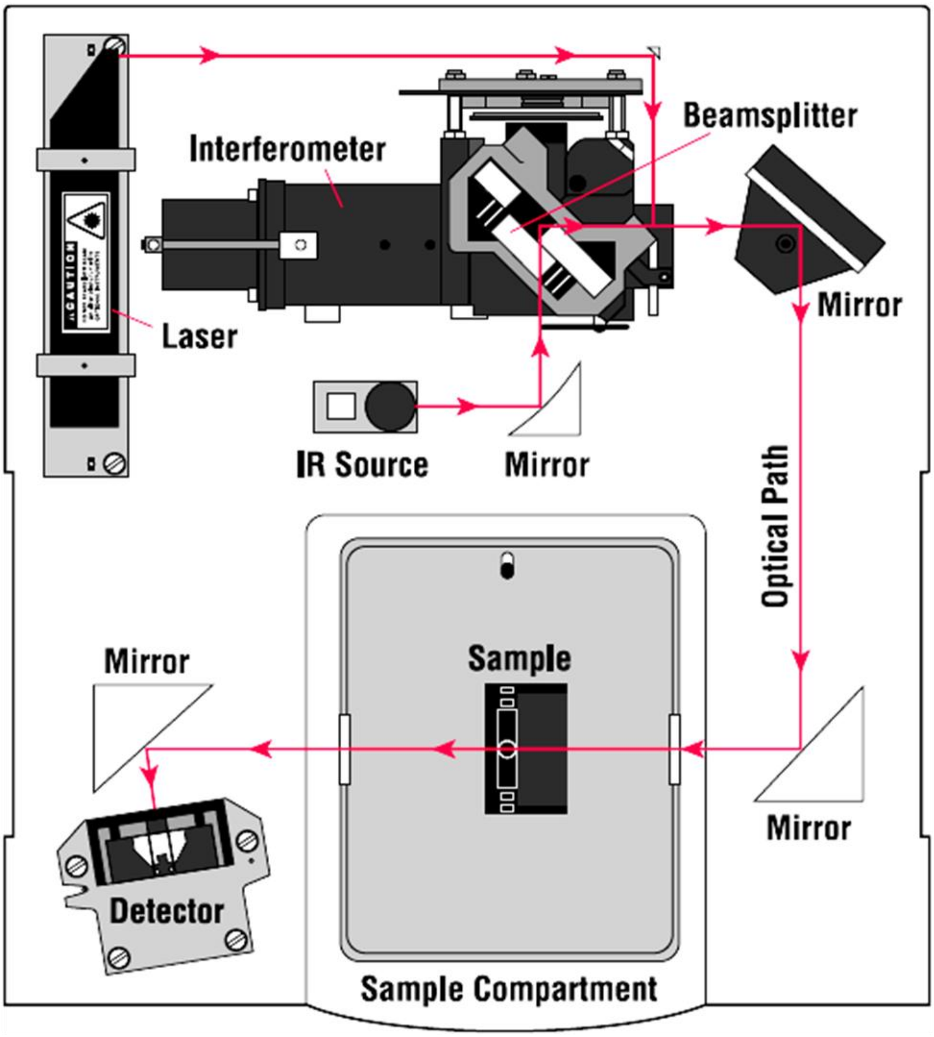

Fig. 3.7. Block Diagram of a typical FT-IR Spectrometer [3].

Fig. 3.8. Image of the JASCO FTIR model 4000

3.3.5 Impedance Spectroscopy

In the present study, ionic conductivity measurements of glass samples were carried out at different temperatures using the impedance spectroscopy (Agilent e4980 LCR meter) in the frequency range of 20Hz to 2MHz. Conducting silver paste was applied on both sides of the glass samples to achieve a controlled contact area for the electrical measurements. At each temperature the sample was maintained for 10 min for thermal equilibration.

3.3.6 Ionic Transport Number Measurements

To confirm a material to be a solid electrolyte, apart from having high ionic conductivity, the charge conduction must be solely due to motion of ions. In other words, the conduction due to electrons should be negligible in comparison to ionic contribution. The transport number measurement of solid materials signifies the contribution of ionic conductivity to the total conductivity. Therefore, it is one of the key factors to be considered while choosing the system as an electrolyte (in super ionic system) or to be used as a cathode material (in mixed conducting system) for battery application. Generally, the ionic transport number has been measured in solid electrolytes using various methods including Wagner’s polarization technique, electrochemical (EMF) measurements, potentiostatic polarization, Tubandt method and DC polarization technique [5]. The electronic contribution to the total conductivity can be obtained from Wagner polarization technique, whereas the other techniques brief about ionic nature of the conducting species. The transport number of a moving charged particle is defined as the ratio of the conductivity due to itself and the total conductivity. There are many methods to ensure the transference number, few of these described below in brief:

I. EMF technique

In this method the ionic conductor is placed between a pair of electrodes of different chemical potentials μ_1 and μ_2. The potential difference (emf) developed across the electrodes is given by [6],

$$E_{obs} = \frac{-1}{F|Z|}\int_{\mu}^{\mu_2} t_i \, d\mu = \frac{t_i\,(\mu_1 - \mu_2)}{F|Z|} = \frac{t_i\,\Delta G}{F|Z|} \qquad \text{……… (3.6)}$$

where t_i is the ionic transport number, μ_1 and μ_2 are chemical potentials of the electrodes, ΔG is the change in free energy involved for a given pair of electrodes, Z is the valence of mobile ion and F is the Faraday's constant. For an ideal electrolyte with $t_i = 1$, the emf generated is given by

$$E_{theo} = \frac{\Delta G}{F|Z|} \qquad \text{……… (3.7)}$$

In the present case, the prepared glass samples are Ag^+ ion conductors and hence the following composition of the cell was fabricated:

Ag** (metal) // **Electrolyte** (glass sample) // **C + I_2 + TMAI ……… (3.8)

where, Ag (metal) acts as anode and cathode consisted of ***C + I_2 + TMAI** (Tetra Methyl Ammonium Iodide)*. The cell reaction for the above constructed cell is as follows,

At anode: $Ag \rightarrow Ag^+ + e^-$

At cathode: $I_2 + 2e^-$ (from load circuit) $\rightarrow 2I^-$ *and*

$2Ag^+$ (through electrolyte) $+ 2I^- \rightarrow 2AgI$

And the standard e.m.f. for this half cell reaction is 0.687 V. And hence the ionic transport number t_{ion} can be calculated using the equation:

$$t_{ion} = \frac{Cell_{e.m.f.}}{0.687} \times 100\,\% \qquad \text{……… (3.9)}$$

II. Wagner Polarization technique

The Wagner's polarization method, which is generally used to determine ionic and electronic transport numbers, is schematically shown in Fig.2.12. In this technique, the sample is placed between two electrode one blocking and the other non-blocking for the mobile ionic species. The sample was polarized under dc bias of constant voltage. Current versus time is monitored for a fixed applied dc potential. The initial current is the total current (i_T), due to the ions (i_i) and electrons (i_e). As the polarization builds up the ionic current, i_i, is blocked and the final current is only due to electrons. The initial total current decreases with time due to the depletion of ionic species in the samples and becomes constant in the fully depleted situation. At this stage, the residual current is only electronic current.

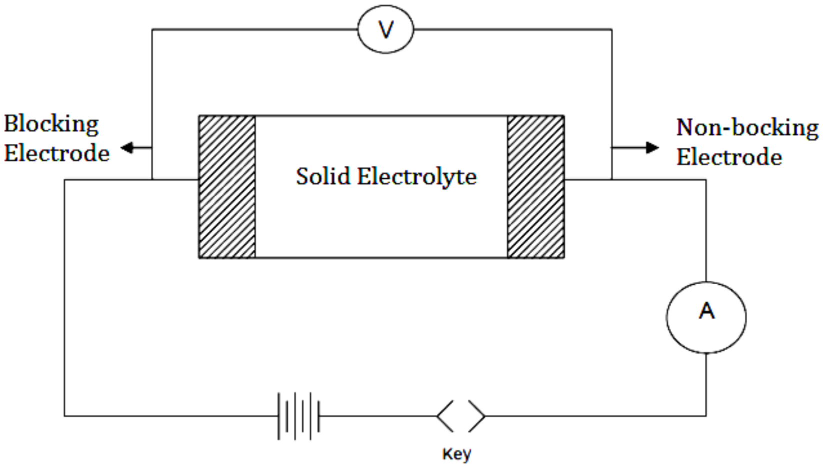

Fig. 3.12. Experimental arrangement of Wagner's polarization method for determining transport number.

The electronic transport number t_e and the ionic transport number t_i respectively are given by

$$t_e = \frac{\sigma_e}{\sigma_T} = \frac{i_e}{i_T} \qquad \text{………} \ (3.10)$$

and $$t_i = 1 - t_e \qquad \text{………} \ (3.11)$$

where, σ_e and σ_T are electronic conductivity and total conductivity respectively, while i_e is the electronic current and i_T is the total current.

III. DC polarization technique

This method was proposed by Evans *et.al.* [7]. According to this technique, **Na-Hg | Solid electrolyte | Na-Hg** type cells are polarized by applying a voltage ΔV = 20 mV for 2h. The initial and final currents are subsequently recorded. Further, as a part of this method, the cells are subjected to ac impedance measurements prior to and after the polarization, and the values of the electrode-electrolyte contact resistances are estimated from the impedance plots. The ionic transport number values are calculated using the expression:

$$t_{Na} = \frac{I_s(\Delta V - R_o I_o)}{I_o(\Delta V - R_s I_s)} \qquad \text{……… (3.12)}$$

where, I_o and I_s are the initial and final current R_o and R_s are the cell resistance/impedance before and after polarization.

Out of these different methods for obtaining the transport number, in the present investigation, EMF technique has been utilized. Keithley 6514 electrometer, interfaced with a personal computer was employed for accurate measurements of e.m.f. of the prepared electrochemical cells.

3.3.7 Solid State Battery Preparation and Allied Studies

The optimum conducting compositions from each glass series were chosen as solid electrolyte for solid state battery application. Solid state battery formation was done as per the configuration given in the section 3.3.6. Characterization and other studies done on thus prepared batteries parameters have been explained in detail in Chapter 6: Solid State Battery applications.

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