CHAPTER-III
MATERIALS PREPARATION AND CHARACTERIZATION TECHNIQUES
III.A MATERIALS PREPARATION

The variety of materials engineered and their technological applications have increased tremendously in recent years. A good number of attempts have been made in the past to develop the solid materials with high ionic conductivity. Some of the important approaches adopted in this respect are listed below.

i) Optimization of preparative parameters [1].

ii) Trapping of high temperature highly conducting phases at ambient temperature using rapid quenching techniques [2,3].

iii) Iso and alio-valent ion substitution [4-6]

iv) Dispersion of second insoluble phase into the otherwise poor ionic conductor [7-10].

The polycrystalline materials have gained much importance owing to isotropy in their electrical and mechanical properties, and ease of preparation in the desired shape and size. Moreover, the polycrystalline samples generally, possess higher conductivity than their single crystalline counterparts [11,12].

The methods suggested in the early stages for the preparation of polycrystalline solid electrolytes are (i) fusing the requisite compositional mixture by solid state reaction at elevated temperature, i.e. sintering [13-15], and (ii) solidification of molten mass of appropriate composition by the process of slow cooling [16-17]. Recently, the conventional cooling such as Al-mould [1], metallic slabs have been used to quench the melt. The rapid quenching techniques such as twin roller [3], copper – drum [18] and splat cooling, developed in the recent past, provide the materials with high defect concentration and reduced grain size. The high defect concentration is expected to facilitate the ionic migration through the solid. Moreover, the minimum grain size, not only offers the high ionic conduction via space charge mechanism as discussed earlier, but also improves considerably the mechanical strength.

The various preparative parameters like pressure of pelletization, temperature and duration of sintering, annealing temperature and quenching have showed
pronounced effect on the electro-physical properties of the samples [1,19]. In spite of a number of advantages in synthesizing solid electrolytes by quenching technique, there still exist many shortcomings. It could result in imparting the undesired colouration, generally, to the sample. Consequently, such a colouration can very well and could hamper the acquisition of useful data of the sample. For example, Raman studies carried out on the particularly quenched sample may give rise to high background intensity, since these samples, in general, tend to burn in a very intense laser beam, eventually affecting the data. The quenching process is usually carried out in an ambient environment, primarily due to limitation of equipment handling. The obvious advantage of having enhanced defect concentration following quenching is more or less annulled by an observed decrease in defect concentration, if the sample is subjected to a number of heating cycles, since the sample tends to attain the most ordered structural state during the process. These factors restrict the utilization of the samples, thus prepared, in technological application such as batteries and sensors. Moreover, it is reported that the high temperature high-conducting phases trapped in Li$_2$SO$_4$ prepared by quenching, disappear with time [20].

On the other hand, the slow cooling synthesis route governs the crystallization of the molten mass of the material due to a much slower $\delta T/\delta t$. As a result, the thermal-history dependent defect concentrations are reduced appreciably. This makes the conductivity parameter almost invariant of the thermal history and shelf life of the sample. A sample, thus prepared, then could be safely utilized and probed in the high temperature application such as sensors, thermal batteries, etc. In the present work the samples were prepared by slow cooling method as described below.

III.A1 METHODOLOGY
The initial ingredients Ag$_2$SO$_4$, BaSO$_4$, CaSO$_4$, and MgSO$_4$ were dried at 200°C for 48 hours. The complete drying of the materials was confirmed by repetitive cycles
of heating and weighing. The weighing of well-dried ingredients was done on an electronic balance (Mattler, AE/63) to obtain appropriate mole ratio with an accuracy of 0.0001g. The dried ingredients with required mole % were then mixed thoroughly under acceptance (wt mixing) with the help of an agate mortar, and followed by second drying process at 150°C for 6-8 hrs.

It needs to be mentioned here that, the samples only up to 60 mole % of BaSO₄, CaSO₄ and MgSO₄ in Ag₂SO₄ were prepared by slow cooling of the melt. The compositions above 60 mole % of BaSO₄, CaSO₄, MgSO₄ in Ag₂SO₄ were prepared following solid state sintering method because Ag₂SO₄ decomposes before melting of mixture.

III.A1.i  Synthesis by Slow Cooling of the Melt

Appropriate compositional mixture were filled in a translucent silica ampoule so as to avoiding any photodecomposition of Ag₂SO₄. Later, the ampoules were heated in an electrically driven, temperature-controlled furnace to a temperature 20°C above the melting point of the mixture. The melt was crystallized by slow-cooling the melt to the room temperature with a pre-determined cooling rate \( \sim 1.5°C/m \). Thus obtained ingots, following a careful retrieval of the sample, were further pulverized to get a very fine powder. The fine powder was palletized isostatically using a Specac make (UK) stainless steel die-punch and hydraulic press at a pressure of 3 tones/cm². The samples were obtained in the form of circular discs of 9mm dia and approximately 1.5mm thick. This synthesis route will hereafter, be referred to as synthesis route III.2 a.


The initial ingredients are dried at 200°C for 48h. The complete drying of the chemicals was confirmed by repetitive cycles of heating and weighing. The weighing of these starting chemicals was done on Mettler (type-AE163) electronic balance, to obtain appropriate mole ratio of the desired compositions with an
accuracy of 0.0001 g. In order to obtain stiochiometric composition, the dried ingredients with required mole % were mixed thoroughly in an agate mortar followed by a second drying process at 150°C for 6-8 hrs.

The well-dried mixture instead of melting in ampoule was palletized uniaxially at 3 tone/cm². The resulting pellets were sintered at a temperature below 20°C of melting temperature of Ag₂SO₄ for 5-6 hours. The sintered pellets were then crushed to fine powder subsequently palletized, and again sintered below 20°C of melting temperature for 5-6 h.

The above process is repeated for 3 or 4 time so as to have well homogenous mixture. This synthesis route will, hereafter, be referred to as synthesis route III.A1.ii

III.A2  COMPOSITIONS

In recent years, a number of electromigration experiments on binary mixture, with a common anion (SO₄, Cl, NO₃, etc), have attracted a great deal of attention, because the binary system shows higher conductivity than pure mono component system [21]. As a matter of fact, the conductivity of the binary system is quite sensitive to the composition. The various compositions for study of binary of Ag₂SO₄ with different divalent sulphate systems (BaSO₄, CaSO₄, MgSO₄) are discussed below.

III.A2.i  SERIES-I: (100-x) Ag₂SO₄-(x)BaSO₄

The synthesis route followed to make compositions listed in table III.1 already discussed in methodology given. In this binary system, Ba⁺² has a larger ionic radius (r = 1.38Å) than that of Ag⁺ (r = 1.26Å). Hence, it was thought quite worthwhile to study the Ag₂SO₄-BaSO₄ binary

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<tr>
<th>Sr.No</th>
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system, particularly, in the backdrop of the study of Ag$_2$SO$_4$-CaSO$_4$ binary system.

The partial replacement of Ag$^+$ by Ba$^{2+}$ cation is especially made with a view to distorting the host lattice of Ag$_2$SO$_4$ while creating extrinsic vacancies on the basis of following formula, Ag$_{2-2x}$M$_x$SO$_4$

III.A2.ii SERIES II : (100-x) Ag$_2$SO$_4$ - (x)CaSO$_4$

Table (III.2) represents various compositions prepared under this series. Apart from the prominence of the general features of aloivalent cation substitution in β-Ag$_2$SO$_4$, the calcium substitution was expectedly more fascinating, since Ca$^{2+}$, generally, known to be responsible for demonstration of anomalous properties of the host system in which it is added. Pertaining to calcium addition it is interesting to note that:

i) Calcium modified BaTiO$_3$ ferroelectric crystal has been known to give anomalous results. The temperature and duration of sintering has been critical in the achievement of a satisfactory combination of density and crystal size of a ferroelectrics compound, which, in turn, modifies the dielectric properties. The sintering process eliminates inter connect, thus facilitating the packing and connected grain growth. The sintering temperature of 1300$^0$C is inadequate to form the single homogeneous phase of pure BaTiO$_3$, but at this sintering temperature, calcium modified BaTiO$_3$ sample exhibits curie temperature. Mitsui and Westphal [22] have pointed out that although calcium concentration has a little influence on the transition temperature, $T_c$, for cubic tetragonal transition in BaTiO$_3$, the lower transition temperature such as the one associated with tetragonal to orthorhombic strongly depends

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<th>Sr.No.</th>
<th>Ag$_2$SO$_4$-CaSO$_4$</th>
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on calcium concentration. In contrast, Zunang et al [23] have reported that Tc depends on the concentration of calcium containing 6 wt % calcium on Ba-site and 5 wt % calcium on Ti-site.

ii) Secondly, it was thought worth while to probe the system, since seemingly the creation of extrinsic vacancies, results in creating additional migrational paths for a mobile Ag⁺ to hop, was expected to promote the ionic conductivity of the system, given that no appreciable modification in the host lattice were to occur upon Ca²⁺ substitution in β-Ag₄SO₄. In crystalline solid electrolytes, appreciable conductivity enhancement can be achieved by optimizing the ratio of mobile ion species and equivalent sites in the sublattice. In general, the number of energetically equivalent sites available should be more than the total mobile ions. On the other hand, the fact that the ionic radius of Ca²⁺ is much smaller \( (r = 0.99\text{Å}) \) than that of the host cation Ag⁺ \( (r = 1.26\text{Å}) \) could lead one to understand the conduction mechanism, particularly, the conduction pathways available to the mobile Ag⁺ in the presence of much smaller guests cation.

Thus, replacement of Ag⁺ by Ca²⁺ is made with a view to distorting the host lattice of Ag₄SO₄ while creating extrinsic vacancies.

### Table III.3: Composition of Series III

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<th>Sr. No.</th>
<th>Ag₄SO₄</th>
<th>MgSO₄</th>
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III.A2.iii SERIES III : \((100-x)\text{Ag}_4\text{SO}_4-(x)\text{MgSO}_4\)

The Table (III.3) represent various compositions prepared under this series. In this binary system Mg²⁺ has a smaller size \( (0.66\text{Å}) \) than of Ag⁺ \( (r = 1.26\text{Å}) \).

The partial replacement of Ag⁺ by Mg²⁺ was made with a view understand the role of lattice distortion of Ag₄SO₄ while creating extrinsic vacancies.
III.B EXPERIMENTAL DETAILS OF CHARACTERIZATION TECHNIQUES

The use of appropriate characterization technique is of paramount importance for a meaningful study. Especially, during the course of the undertaken study, it was absolutely vital to determine and analyze the solid solubility limits of various cations, to identify and verify different phases in the bulk sample, to investigate the changes, if any, that take place in the lattice parameter values, and to study the structural changes along with the surface morphology. During the present work, following characterization techniques were employed.

i) Differential scanning calorimetry (DSC) technique to predict the solid-solid phase transition temperature $T_c$, enthalpy $\Delta H$ of phase transition and melting point up to $600^\circ$C.

ii) Differential thermal analysis (DTA) to obtain the value of solid-solid phase transition temperature $T_c$ and melting point $T_m$ at very high temperature ($1100^\circ$C), since upper limit of DSC is only $600^\circ$C.

iii) X-ray powder diffraction (XRD) technique to determine and analyze the solid solubility to confirm or rule out the presence of various phases (bi-phase mixture) present in the solid electrolyte. The rigorous analysis of the obtained data also gives quantitative information on the lattice parameters, the comparison of which with that of the host samples yields very vital information on the effect of ionic size by virtue of addition of the guest cation to the host system.

iv) Infrared (IR) spectroscopy / Fourier transform infrared (FTIR) spectroscopy technique to analyze the finer structure influence on antagonist ion of the samples.

v) Scanning electron microscopy (SEM) technique to study the surface morphology of the materials, and to identify the particular composition deciding the limit to the formation of solid solution. Additionally, to
obtained the information towards grain morphology, size and their
distribution in the sample.

III.B1 THERMAL ANALYSIS
Taken through a wide range of temperatures, a substance may undergo physical and
chemical changes, react with the ambient atmosphere or jettison water of
crystallization and other fragments. All such changes are accompanied by the
absorption or release of energy in the form of heat. Some changes involve a weight
gain or loss and then may be thermo mechanical or electrical conductivity changes.
The rate and temperature at which materials undergo physical and chemical
transitions as they are heated/coolcd, and the energy as well as the weight changes
involved is the subject of thermal analysis. Since DSC and DTA techniques were
used to obtain the thermal parameters of various compositions belonging to three
series, discussed above, the details of both these techniques are given below.

III.B1.i Differential Scanning Calorimetry (DSC)
In DSC, the sample and the reference materials are subjected to a closely
controlled-programmed temperature (Fig. III.1). In the event that a transition occurs
in the sample, however, thermal energy is added to or subtracted from the sample or
reference containers in order to maintain both the sample and reference at the same
temperature. Because this energy input is precisely equivalent in magnitude to the
energy absorbed or evolved in a particular transition. The recording of this
balancing energy yields a direct calorimetric measurement of the energy associated
with the transition. The information obtained from this technique, coupled with
thermomechanical analysis, x-ray diffraction patterns, and chemical analysis of the
residues and any evolved gases, provides a quantitative and qualitative estimation of
solid-state reactions. Depending on whether process is exothermic or endothermic
one gets a maximum or minimum in the thermogram. The characteristics
Fig III.1: Arrangement of temperature sensor in differential scanning calorimetry (DSC)

temperature of the physical/chemical process is taken at the onset of the peak in case of endothermic process, and the peak temperature for exothermic process.

The DSC thermograms at ambiance for the test samples of size 30-50 mg were recorded (RSIC, Nagpur University, Nagpur) to study changes in solid-solid phase transitions, heat of transition, etc. using Mettler TA 4000, DSC 25 at a heating rate of $10^0\text{C/min}$.

III.B1.ii Differential Thermal Analysis (DTA)
Differential thermal analysis finds a wide application in the identification and characterization of materials. Particularly, it is considered to be a unique technique for obtaining the vital information about the specific chemical or physical change that is accompanied, either by evolution or absorption of heat in a test material during heating or cooling. Le Chatelier used this technique for the first time in 1887 to investigate the thermal behaviour of clay.

In conventional DTA, test sample and reference materials are placed close together in an environment, which is heated or cooled precisely at the pre-selected rate. As the environmental temperature is changed, the temperature of sample and
reference also undergoes a change. In the absence of physical or chemical change, the temperature difference $\Delta T$ (sample temperature minus reference temperature) remains zero, i.e. $\Delta T=0$. When temperature of environment reaches a point, where a physical or chemical changes occurs in the test sample then $\Delta T$ no longer remains zero. The temperature difference between these two (reference and test samples) is recorded, which gives a peak in a plot of $\Delta T$ against time/temperature. Depending on whether the process is exothermic or endothermic, one gets a maximum or minimum in the thermograms.

As soon as a transition starts in the sample, a certain amount of heat can be absorbed or given up before the sensitivity of the apparatus allowed it to be detected by the differential thermocouple. Therefore, the first deviation of DTA-curve from the base line has been taken as more appropriate representative of the start of the transition than the peak maximum as shown in figure III.2. However, a peak temperature has been taken as a transition temperature in the case of exothermic process. Besides, the position of peak maximum has been found to shift with a change of heating rate. A change in particle size and packing of the sample can be important in DTA, because the estimated transition temperature and the position of the peak maximum changes, accordingly.

The shape of the peaks is affected by the amount of sample and heating rate. Interestingly the area of the peaks depends on the sample amount in such a way that

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Fig. III.2: Determination of transition temperature $T_1$, $T_2$, and $T_3$.}
\end{figure}
a large amount of salt gives peaks with large areas and vise-versa. A high heating rate gives high but narrow peaks and low heating rate gives low and wide peaks, the area being constant. If the amount of sample and the heating rate are kept constant, valuable information on the phase diagram can be obtained from the shape of the peaks.

The DTA thermograms for the test samples were recorded using Perkin Elmer, DTA 1700/TADS high temperature thermal analyzer, during the heating cycle. Essentially, a thermal run of each sample is taken in the nitrogen atmosphere in order to avoid the oxidation of the sample.

III.B2 X-RAY POWDER DIFFRACTION (XRD)

It is a well-established fact that every crystalline material gives a unique x-ray diffraction pattern (comparable with a fingerprint) with a very few exceptions. A careful study of diffraction patterns of unknown materials offers a powerful means of qualitative identification of various phases present therein. It is, therefore proved to be a quick and non-destructive method for an identification of compounds. In addition to this, the information obtained on lattice parameters using the x-ray powder diffraction data, gives better insight to structural changes produced in compound by physical or chemical processes. These merits put this technique above all. which are, in general, used for structural characterization of materials.

In the present work, x-ray powder diffraction data were analyzed in a greater detail with a view to understand the basic factors, which would be influencing ionic conductivity in solids and various phases.

The room temperature x-ray powder diffraction data for all samples, under study were recorded at R.S.I.C. Nagpur (INDIA) with the help of Philips PW 1700 x-ray diffractometer. Details of the operating conditions are as mentioned below:

i) Generator Setting : 350 kV 20 ma

ii) Monochromater : Curved graphite crystal

iii) Theta compensating slit : Fixed at 1 deg. Divergence/
analysis is better method for these determinations. Nevertheless, x-ray diffraction has been well suitable for the determination of solvus (solid solubility) curves.

III.B2.ii Structure Determination
It is well known that x-ray diffraction gives a possible means of determining the various phases involved in a phase diagram. If the investigated phase is pure cubic, the determination will be rather easy (Fig. III.4). Because, a cubic lattice gives a very few diffraction lines arranged in such a way, that sometimes just a glance at the diffractogram will tell us the structure is simple cubic, body centered cubic,
face-centered cubic, or diamond cubic (Fig. III.4). Also Indexing of the lines in this
case is always fairly easy.

Diffraction lines from substances belonging to the uniaxial system
tetragonal, trigonal and hexagonal) are more difficult but can usually indexed. The
trouble involved increases with increasing unit cell size, which lead to a larger
number of lines. An orthorhombic diffractogram pattern may prove to be very
troublesome, especially, if the unit cell is large. The monoclinic and even more the
triclinic, system presents the greatest difficulty because of the larger number of
variables involves [24-26].

III.B3 INFRARED (IR) SPECTROSCOPY/FOURIER TRANSFORM
INFRARED (FTIR) SPECTROSCOPY
The broadband spectra like Raman and IR are presently becoming more popular as
the tools to study the structural aspects sensitive to change in compositions. In
Raman spectroscopy, Raman spectra result from interaction of incident light with
energy levels of the system. The incident light causes an induced polarizability
represented by

\[ P = \left[ \alpha_0 + \alpha_{\text{vib}} \cos (2\pi v_{\text{vib}}) \right] [E^0 \cos(2\pi v_0 \theta)] \]  \hspace{1cm} (III.1)

Getting three terms given by

\[ P = \alpha_0 E^0 \cos(2\pi v_0 \theta) \] Raleigh scattering +
\[ \alpha_{\text{vib}} E^0 \cos \left[ 2\pi \left( v_0 - v_{\text{vib}} \right) \right] \text{Raman (Stoke’s Scattering)} +
\[ \alpha_{\text{vib}} E^0 \cos \left[ 2\pi \left( v_0 + v_{\text{vib}} \right) \right] \text{Raman (anti-stoke’s Scattering)} \]  \hspace{1cm} (III.2)

The appearance of additional frequencies, represented by \( v_0 + v_{\text{vib}} \) and \( v_0 - v_{\text{vib}} \),
constitutes. Raman scattering. Here, \( v_0 \) represents the incident frequency and \( v_{\text{vib}} \)
gives the energy difference between the vibrational energy levels of the interacting
system. The additional frequencies always appear in pairs. Raman scattering is very
weak phenomenon, and therefore the use of powerful monochromatic laser light
along with powerful light-gathering techniques becomes important. Typically, if 30,000 photons are incident on a 1 m thick solid, one scattered photon will represent a Raman effect. Thus, very intense incident light has to be used to ensure sufficiently intense Raman lines. The use of a particular monochromatic laser source provides this intensity. Another approach, however, is to use very sensitive light-gathering and light-counting techniques by the use of CCD cameras or charge-coupled devices, which is infeasible many a time. This technique, when specially coupled with infrared studies gives valuable structural information, which can rarely be obtained otherwise.

Infrared spectroscopy, particularly, involves the absorption of the electromagnetic radiations by matter. The existence of these radiations has been known since long time with the discovery of Sir William Herschel in 1800 [27]. Today, the infrared spectroscopy is understood to include the region of the electromagnetic spectrum of approximately 0.78 μm (1/λ = 12500 cm⁻¹) to 1000 μm (1/λ = 10 cm⁻¹). In 1903, Colbentz [28] started a series of investigations, which included hundreds of substances of organic and inorganic nature. It was Colbentz [28] who recognized the existence of absorption frequencies as a characteristic of specific organic or inorganic molecular structure, and also laid the foundation of modern group and vibration analysis.

The most useful segment of infrared region of the spectrum is from 2 to 16 μm. The absorption bands that occur in this region are due to the fundamental molecular vibrations. As a consequence, they lend themselves to identification, qualitative analysis and band assignment.

It is well-accepted fact that the matter absorbs infrared radiations selectively with respect to wavelength. The two necessary conditions, which must be meet before the absorption of infrared radiations by the molecules can occur, are:

i) There must be a change in dipole moment of a molecule, and this will occur only when the electrical charges on the atom are unequally distributed.

Under these conditions, a stationary alternating electric field is produced
Fourier transform, we can reconstruct all the waves that went into making it up. The interferogram can be viewed as being a complex wave, since all of the IR frequencies are added together in the modulator and then subtracted some through absorption in the sample. By subjecting the interferogram to a Fourier transform, one gets back all of the original frequencies, minus those that were partially or totally absorbed by the sample. In effect we reverse the modulation produced by the interferometer. By creating a graph of the intensity of each frequency, one get the spectrum of the sample. Another way to look at this is to think of the modulator as converting the frequency domain of the IR source to the time domain of the interferogram. But for the information to be useful, we need to convert it back to the frequency domain. This is what the Fourier process does.

III.B4 SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscopy has been the most versatile technique, judged by its widespread use in almost all branches of science, and more appropriately by the importance of the information, which it has provided. The SEM is claimed as a significant scientific technique for characterization. In addition to this, the most important advantage of SEM is due to its excellent resolution when compared with that of the optical microscope. Vastly increased depth of focus in this technique is also of a special value. Indeed, the advantages highlighted above, of SEM have paved the way exceptionally to study the morphology of materials.

The results of x-ray powder diffraction analysis have indicated, in general, the bi-phase mixture identification in most of the samples, under investigation. Thus, the SEM technique was employed for characterization of the material from the point of view of understanding the macroscopic aspects such as the particle size, phase assemblage, grain-boundaries, voids and the distribution of impurity phases.

The macrostructural examination of the samples was carried out with the help of a Stereo scan 250 Mark 111, Cambridge (UK) scanning electron microscope. Mounting them on an aluminum stub with DUCO cement, and
applying silver paint around the edge of each specimen and the stub prepared the specimens for the SEM study. Later, they were transferred to a vacuum jar and coated with a conductive layer of gold using sputtering unit. The photography of the surface was performed with Polaroid system.

III.B5 HARDNESS TESTING

The mechanical strength of pellet is important property of material, which is used in a sensor and play a important role in product development and control in sensor operation. It has been described by various terms including friability, hardness, fracture resistance, crushing strengths or breaking strength.

The hardness test roughly classified into three types: The indentation hardness test, the dynamic hardness test and the scratch hardness test. The indentation hardness test has been most commonly used now a day. This test penetrates a permanent deformation on the test piece surface using an indenter of the diamond or other rigid body and determines the hardness of the test piece based on the load use to generate the deformation and the dimensions of the generated deformation. Commonly used methods include Vickers hardness, Rockwell hardness and Brinell hardness.

Vickers hardness is determined based on the test load used when penetrating a Vickers indenter on the test piece surface, and the indentation area calculated from the indented diagonal length. Vickers hardness HV is usually calculated following relation

\[ HV = 1.854 \frac{F}{d^2} \]  

(III.3)

where, \( HV \), \( F \) and \( d \) are Vickers hardness, test load (kgf) and mean of the indentation diagonal length (mm), respectively. Note that \( HV \) requires no unit. The samples under present investigation were subjected to Vickers hardness testing using JIS B 7734-1983 (USA) hardness tester at VNIT, Nagpur.
III.C ELECTROCHEMICAL SENSOR: Fabrication and Characterization Techniques.

New electrochemical methods of sensing various gases present in the environment/atmosphere have attracted many scientists and engineers due to inherent simplicity, direct readout and scope for miniaturization [6]. The use of electrochemical gas sensors is based upon the fundamental physical properties associated with the sensing species, which develop the cell emf in logarithmic proportion of the concentration of the particular gas in parts per million (ppm).

Electrochemical cells with following general configuration were fabricated by pressing the reference electrode and electrolyte under vacuum using stainless steel die-punch at the pressure 5 ton/cm²

Solid reference(Ag+Ag₂SO₄) // electrolyte // Pt (Test gas).

The diameter and thickness of sensor were 8 and ≈2 mm, respectively. The eutectic of each binary system, on the basis of

![Fig. III.5: Schematic of electrochemical cell.](image)

![Fig. III.6: Sensor probe assembly.](image)

high ionic conductivity, is used as solid electrolyte to realize potentiometric sensor. The platinum film on the flat surface of auxiliary electrolyte was obtained using dc/rf sputtering. The cell is shown schematically in figure III.5. The designed and developed probe assembly for sensor characterization is shown schematically in figure III.6. Essentially, it consists of outer
quartz u-shaped jacket fitted with a flange made out of flexi-glass. The quartz tube having inlet and outlet having appropriate flexi-glass flange fits into the flange of outer jacket ensuring the no gas leakage. A pressing rod attached with stainless-steel spring at the top and platinum mesh at bottom was arranged to provide good electrical contacts at test side of electrochemical cell. The lower platinum electrode was supported with a piece of quartz tube. The platinum wires fused to platinum electrode facilitating emf measurements. Following aspects were chiefly considered during the designing and fabrication of the probe. (i) Gas leak proof compartments for reference and sensing electrodes. (ii) Spring loading to compensate the change in dimension of pellet during heating and cooling processes. (iii) Operated at about 550 °C. (iv) Reusable. (v) Sufficient catalytic area, etc.

As a matter of fact, evaluation of any device under development demands very sensitive and reliable testing/characterization instrumentation. A little discrepancy/ inaccuracy during the testing leads to wrong conclusions and impedes greatly the progress of the development work. Thus, it is very crucial to characterize the sensors using infrastructure having high reliability. The experimental setup for sensor characterization used in the present investigation is shown schematically in figure III.7. Some of the crucial stages viz. sensor heating, gas mixing, and high impedance data acquisitions were handled with immense care.

The temperature of the cell, during the characterization, was maintained closed to 500 ±1°C using Eurotherm 810 PID temperature controller. A blend of appropriate percentage of CO₂/SO₂ gas, while keeping oxygen 21% and remaining carrier argon gas (78%), was obtained with the help of flow-meters (Teledyne Hastings, USA) and gas-mixing sub-system (Fig. III.7) The pre-decided test gas was allowed to flow through the probe assembly. Simultaneously, the variation of cell emf was recorded as a function of time after every 10 seconds using Solatron electrochemical interface or Keithley 617 programmable electrometer or Keithley 236 SMU. The concentration of the gas is toggled from x₁ to x₂ ppm and subsequently, the open circuit voltage (OCV) as a parametric function of time was
Fig.III.7: A block diagram of the multi-sensor characterization workstation

recorded to determine the response time and reversibility of sensor. In order to check the cross interference of other gases, the sensor was exposed to standard gas mixtures containing impurity gases.

The electrical conductivity determination plays a crucial role in any study pertinent to solid electrolyte, in general, and solid-state electrochemical devices, in particular. Therefore, the details of techniques used for electrical characterization, obtained results followed by discussion are taken up in the succeeding chapter.
REFERENCES