Chapter - 3

Synthesis an Characterization Methods

3.1 Introduction

Synthesis and development of materials with desired properties is of utmost important in experimental condensed matter physics and its research. The samples can be synthesized in variety of forms, shapes and size such as single crystals, amorphous solids, thin films, thick films, polycrystalline powder, etc., depending upon the objectives of research.

Various synthesis methods are used depending upon the need, purpose of research, product required, underlying assumptions, parameters to be studied, etc. Each method has its own advantages and limitations. Some of the methods available to synthesize good quality of samples in bulk and nano forms include Solid State Reaction (SSR), Vapor Phase Transport (VPT), Precipitation, Co-precipitation, Sol - Gel, Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD), Chemical Solution Deposition (CSD), Metal-Organic Chemical Vapor Deposition (MOCVD), Sputtering, Flux Growth Technique and Electrochemical Methods.

The choice of synthesis method is an important criterion for every research. Low cost process with desired characteristics of the materials as well as the need of the industry and market drives the choice of synthesis method and other issues in research.

In this study, the samples have been synthesized using the Solid State Method and the Precipitation Method. Both these methods are economical in time as well as cost. The former method gives bulk material while the latter can be suitably controlled to get samples either in bulk or nano form.

Synthesis of Lanthanum Sulphide, Cerium Sulphide, Gadolinium Sulphide and Yttrium Sulphide was carried out with Europium, Terbium and Manganese as dopants. The doping percentages were taken to be 1%, 2% and 3%.

A total of 80 samples, 40 by Solid State Method and 40 by Precipitation method have been synthesized.

3.2 Solid State Method

The **solid-state reaction route** is the most widely used method for the preparation of polycrystalline solids from a mixture of precursors, generally in solid state. It provides a large range of selection of starting materials like oxides, carbonates, nitrates, etc. Solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often to 1000 to 1500 °C in order for the reaction to occur at an appreciable rate.

Figure 3.1: High Temperature Muffle Furnace at Department of Nanoscience and Advanced Materials, Saurashtra University, Rajkot in which samples were synthesized using Solid State reaction.

The factors on which the feasibility and rate of a solid state reaction depend include, reaction conditions, structural properties of the reactants, surface area of the solids, reactivity and thermodynamic parameters associated with the reaction [1,2]. In solid state reactions, the reactants have only restricted access to each other as compared to the reactions in fluids where intimate contact between reactant molecules is a natural consequence of the kinetic nature of reactants. In solid state reactions, at least one reactant must diffuse into the other in order that the reaction may be initiated and propagated. Hence, the precursors need to be grinded and mixed thoroughly.

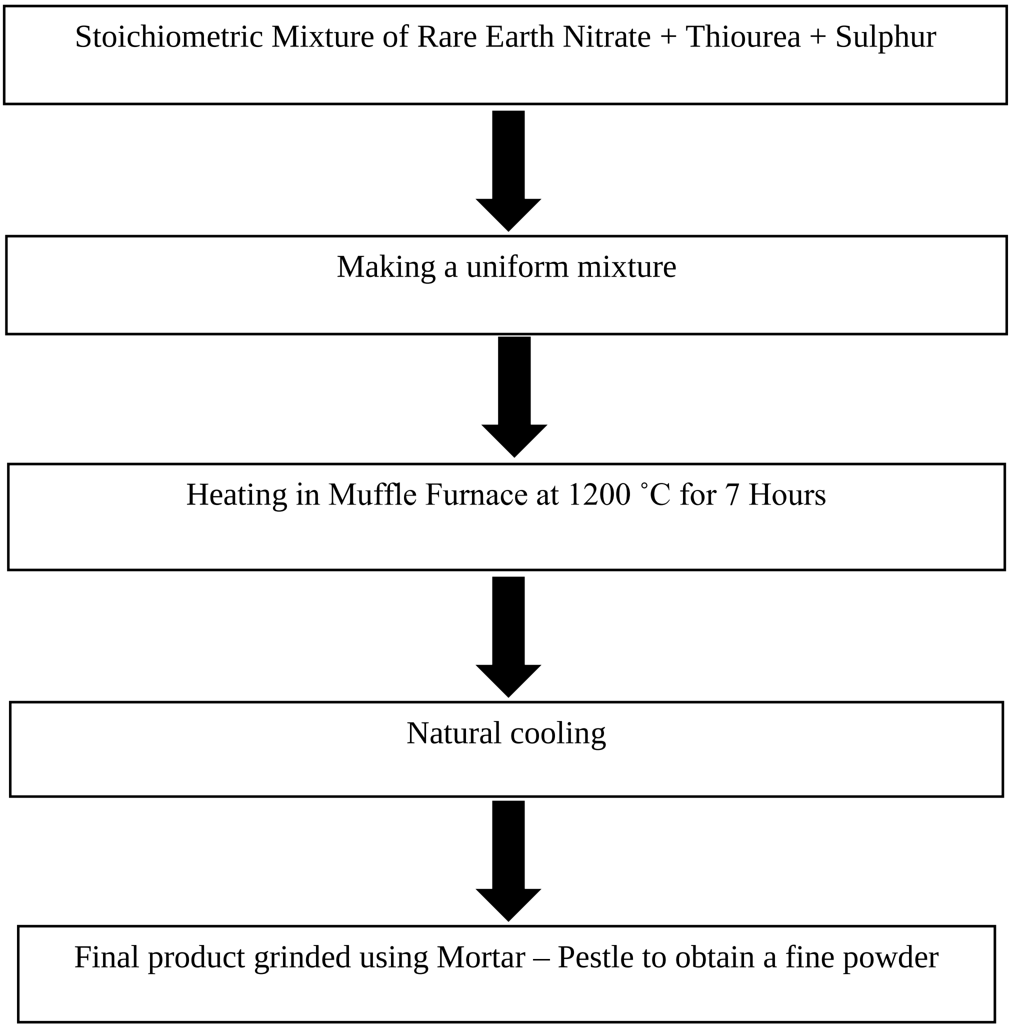
The main point on which chemical reaction in solids distinguishes themselves from those occurring in liquids or gaseous phases are the effects of lattice structure and diffusion mechanism [3]. Whether it is transformation of crystal structure or formation of chemically different solid, these involve rupture of old bonds and formation of new ones to form products [4]. Solid state reactions involve two stages. The first stage of reaction is the formation of nuclei of the product and the second stage is the growth of the product layer.

This nucleation may be difficult because of (a) the considerable differences in structure between reactants and product and (b) the large amount of structural reorganization that is involved in forming the product. Although nucleation is a difficult process, the subsequent stage, involving growth of the product layer is more challenging. For further reaction to occur and the product layer to grow thicker, counter diffusion of ions must occur right through the existing product layer. Thus, both thermodynamic and kinetic factors are important in SSR.

In SSR method, the solid reactants react chemically without the presence of any solvent at high temperatures yielding a product which is stable. The major advantage of SSR method is that the final product in solid form is likely to be structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and nontoxic for the development of rare earth sulphides.

In order to facilitate the sulphide reaction, it is a practice to use Hydrogen Sulphide (H_2S) or Carbondisulphide (CS_2) or the entire reaction is carried out in an inert gas atmosphere of Argon (Ar). However, in the present synthesis, none of the above toxic gases were used and successful synthesis of rare earth sulphides has been achieved by a simple high temperature heating reaction.

The raw materials which were used include 99.9% Cerium Nitrate Hexahydrate (Loba Chemie), 99.9% Gadolinium Nitrate Hexahydrate (CDH), 99% Lanthanum Nitrate Hexahydrate (Loba Chemie), 99.9% Yttrium Nitrate Hexahydrate (CDH), 99.9% Manganese Nitrate Tetrahydrate (Sigma Aldrich), 99.9% Europium Nitrate Hexahydrate (CDH), 99.9% Terbium Nitrate Pentahydrate (CDH), 99% Thiourea (Loba Chemie) and AR grade Sulphur (Loba Chemie).



Flowchart of Synthesis by the Solid State Method

3.2.1 Synthesis of undoped and doped (1%, 2% and 3% Mn, Eu, Tb) samples of Cerium Sulphide (Ce_2S_3), Gadolinium Sulphide ((Gd_2S_3), Lanthanum Sulphide (La_2S_3) and Yttrium Sulphide (Y_2S_3) by Solid State Method

To get an undoped sample, stoichiometric amounts of Cerium Nitrate Hexahydrate [$Ce(NO_3)_3.6H_2O$] /Gadolinium Nitrate Hexahydrate [$Gd(NO_3)_3.6H_2O$] /Lanthanum Nitrate Hexahydrate [$La(NO_3)_3.6H_2O$] /Yttrium Nitrate Hexahydrate [$Y(NO_3)_3.6H_2O$], Thiourea (NH_2CSNH_2) and Sulphur were taken and mixed well till it became a uniform mixture. This mixture was kept in a silicon crucible and heated in a muffle furnace at 1200 ˚C for 7 hours.

The furnace was allowed to cool and then the mixture was taken out. The mixture was ground using mortar and pestle to get a fine powder as the final product.

In order to synthesize 1%, 2% and 3% Mn, Eu and Tb doped Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3, appropriate amount of Nitrates of dopants i.e. Manganese Nitrate [$Mn(NO_3)_2.4H_2O$], Europium Nitrate [$Eu(NO_3)_2.6H_2O$] and Terbium Nitrate [$Tb(NO_3)_2.5H_2O$] were added to the precursors mentioned above and the mixture was heated in a muffle furnace at 1200 ˚C for 7 hours. The furnace was allowed to cool naturally and then the mixture was taken out. The mixture was ground using mortar and pestle to get a fine powder as the final product.

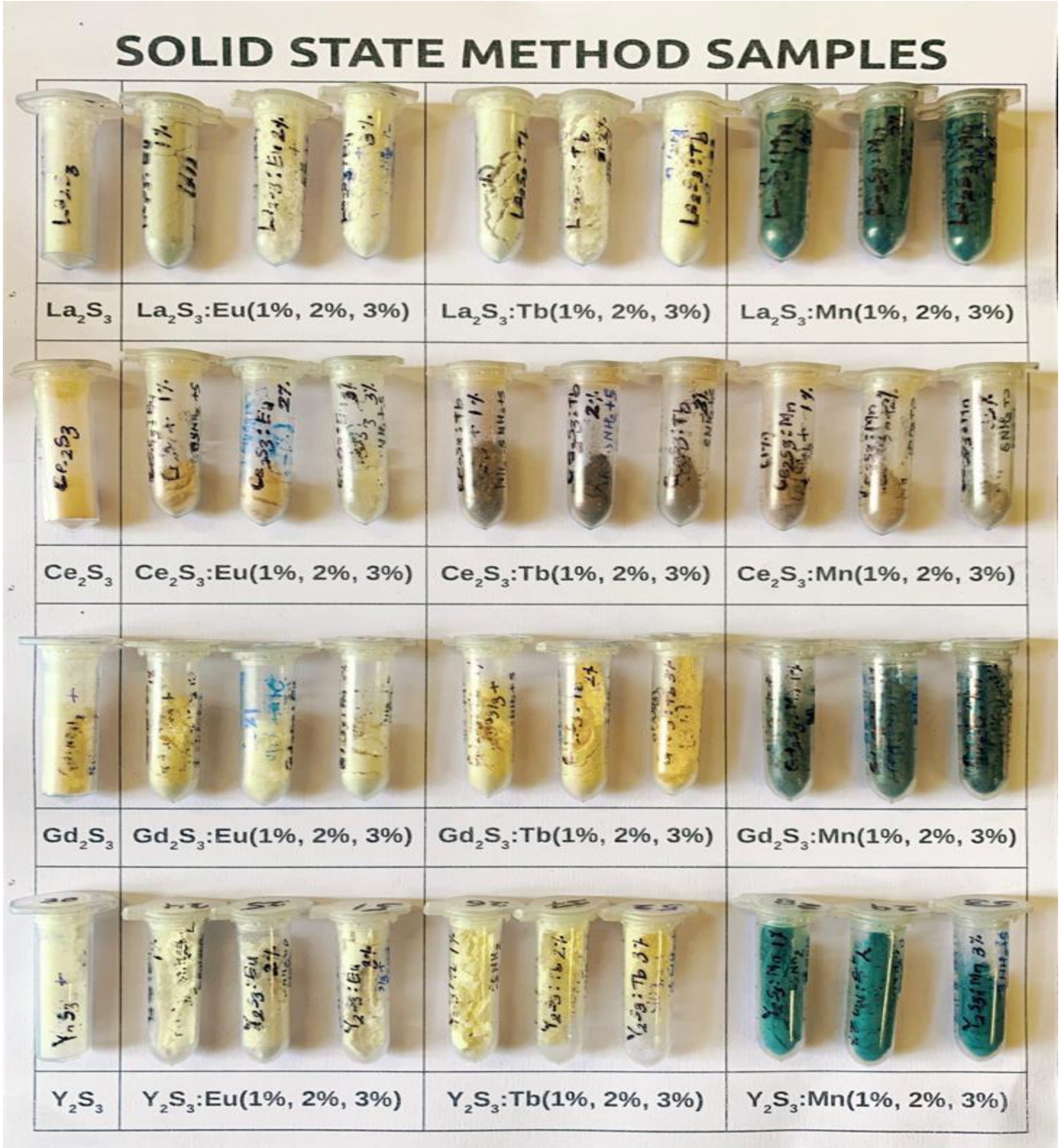


Figure 3-2: Samples Synthesized by Solid State Method

Table 3-1: Coding for samples synthesized by Solid State Method

Sr. No.	Sample Name	Sample Code
1	Ce_2S_3 Undoped	CeU-SS
2	Ce_2S_3 1% Mn Doped	CeM1-SS
3	Ce_2S_3 2% Mn Doped	CeM2-SS
4	Ce_2S_3 3% Mn Doped	CeM3-SS
5	Ce_2S_3 1% Eu Doped	CeE1-SS
6	Ce_2S_3 2% Eu Doped	CeE2-SS
7	Ce_2S_3 3% Eu Doped	CeE3-SS
8	Ce_2S_3 1% Tb Doped	CeT1-SS
9	Ce_2S_3 2% Tb Doped	CeT2-SS
10	Ce_2S_3 3% Tb Doped	CeT3-SS
11	Gd_2S_3 Undoped	GdU-SS
12	Gd_2S_3 1% Mn Doped	GdM1-SS
13	Gd_2S_3 2% Mn Doped	GdM2-SS
14	Gd_2S_3 3% Mn Doped	GdM3-SS
15	Gd_2S_3 1% Eu Doped	GdE1-SS
16	Gd_2S_3 2% Eu Doped	GdE2-SS
17	Gd_2S_3 3% Eu Doped	GdE3-SS
18	Gd_2S_3 1% Tb Doped	GdT1-SS
19	Gd_2S_3 2% Tb Doped	GdT2-SS
20	Gd_2S_3 3% Tb Doped	GdT3-SS
21	La_2S_3 Undoped	LaU-SS
22	La_2S_3 1% Mn Doped	LaM1-SS
23	La_2S_3 2% Mn Doped	LaM2-SS
24	La_2S_3 3% Mn Doped	LaM3-SS
25	La_2S_3 1% Eu Doped	LaE1-SS
26	La_2S_3 2% Eu Doped	LaE2-SS
27	La_2S_3 3% Eu Doped	LaE3-SS
28	La_2S_3 1% Tb Doped	LaT1-SS
29	La_2S_3 2% Tb Doped	LaT2-SS
30	La_2S_3 3% Tb Doped	LaT3-SS
31	Y_2S_3 Undoped	YU-SS
32	Y_2S_3 1% Mn Doped	YM1-SS
33	Y_2S_3 2% Mn Doped	YM2-SS
34	Y_2S_3 3% Mn Doped	YM3-SS
35	Y_2S_3 1% Eu Doped	YE1-SS
36	Y_2S_3 2% Eu Doped	YE2-SS
37	Y_2S_3 3% Eu Doped	YE3-SS
38	Y_2S_3 1% Tb Doped	YT1-SS
39	Y_2S_3 2% Tb Doped	YT2-SS
40	Y_2S_3 3% Tb Doped	YT3-SS

3.3 Precipitation Method

In conventional synthesis routes, the reactants are mixed together by manually grinding the mixture of starting materials or mechanically by ball milling process. The subsequent reaction rate depends on a large degree on the particle size of the reactants, the degree of homogenization achieved on mixing and the intimacy of contact between the grains as well as the obvious effect of temperature.

Figure 3-3: Precipitation Reaction Apparatus at M. M. Patel Science and Research Institute, Kadi Campus, Gandhinagar used to synthesize samples.

By using the Precipitation route, it is possible to achieve a high degree of homogenization together with a small particle size and faster reaction rates. The extent to which a component can be separated from solution can be determined from the solubility-product constant obtained by determining the quantity of dissolved substance present in a known amount of saturated solution. This value is known as the solubility. The solubility can be drastically altered merely by adding to the solution any of the ions which make up the precipitate. Although, solubility can be altered over a wide range, the solubility product itself remains practically constant over the same range.

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids. They either remain suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

Most precipitation reactions are single replacement reactions or double replacement reactions [5]. In a single displacement reaction, a compound reacts with an element, and the more reactive element displaces the less reactive element of the compound.

$$XY + Z \rightarrow XZ + Y \quad \text{OR} \quad YZ + X$$

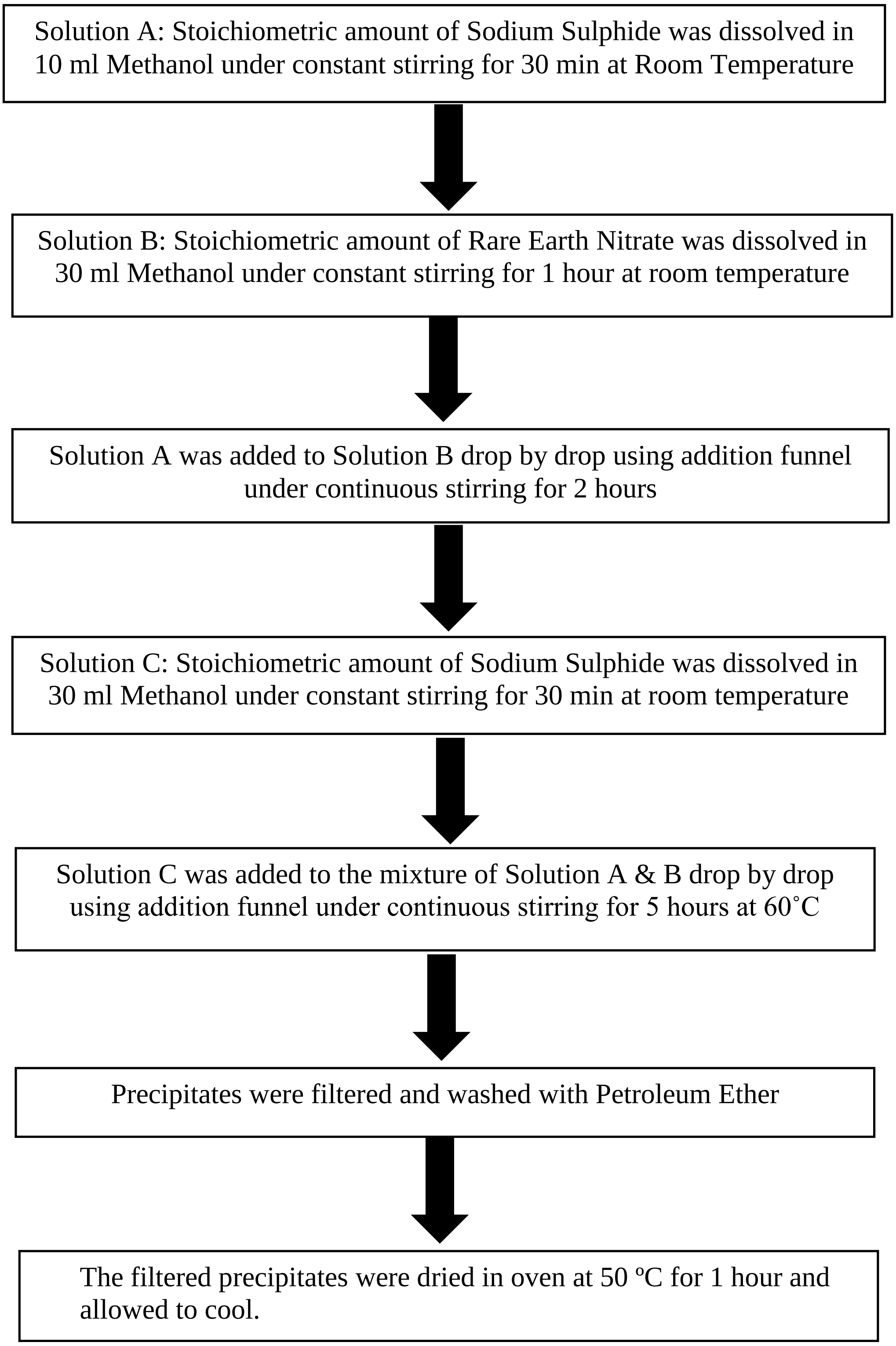
A double displacement reaction is a chemical reaction in which two compounds react with each other, and one component from each reacting compound is exchanged to form the product. During this reaction, the anions and cations of both the compounds switch places to form two new compounds.

$$XY + ZA \rightarrow XA + YZ$$

In this study, undoped rare earth sulphides of Cerium, Gadolinium, Lanthanum and Yttrium and those doped with Manganese, Europium and Terbium have been synthesized by double replacement reactions. The general equation for these reactions is as given below:

$$2Ln(NO_3)_3 + 3Na_2S \rightarrow Ln_2S_3 + 6NaNO_3 \quad \text{where } (Ln = Ce, Gd, La \text{ and } Y)$$

The raw materials used included 99.9% Cerium Nitrate Hexahydrate (Loba Chemie), 99.9% Gadolinium Nitrate Hexahydrate (CDH), 99% Lanthanum Nitrate Hexahydrate (Loba Chemie), 99.9% Yttrium Nitrate Hexahydrate (CDH), 99.9% Manganese Nitrate Tetrahydrate (Sigma Aldrich), 99.9% Europium Nitrate Hexahydrate (CDH), 99.9% Terbium Nitrate Pentahydrate (CDH) and AR grade Sodium Sulphide (SDFCL).



Solution A: Stoichiometric amount of Sodium Sulphide was dissolved in 10 ml Methanol under constant stirring for 30 min at Room Temperature

Solution B: Stoichiometric amount of Rare Earth Nitrate was dissolved in 30 ml Methanol under constant stirring for 1 hour at room temperature

Solution A was added to Solution B drop by drop using addition funnel under continuous stirring for 2 hours

Solution C: Stoichiometric amount of Sodium Sulphide was dissolved in 30 ml Methanol under constant stirring for 30 min at room temperature

Solution C was added to the mixture of Solution A & B drop by drop using addition funnel under continuous stirring for 5 hours at 60˚C

Precipitates were filtered and washed with Petroleum Ether

The filtered precipitates were dried in oven at 50 ºC for 1 hour and allowed to cool.

Flow Chart of Synthesis by Precipitation Method

3.3.1 Synthesis of undoped and doped (1%, 2% and 3% Mn, Eu, Tb) samples of Cerium Sulphide (Ce_2S_3), Gadolinium Sulphide ((Gd_2S_3), Lanthanum Sulphide (La_2S_3) and Yttrium Sulphide (Y_2S_3) by Precipitation Method

0.01 mole of Sodium Sulphide [Na_2S] was dissolved in 10 ml of Methanol [CH_3OH] by constant stirring with the help of mechanical stirrer for 30 minutes at room temperature to prepare solution A.

Another Solution B was prepared by dissolving 0.04 mole of Cerium Nitrate Hexahydrate [$Ce(NO_3)_3.6H_2O$] /Gadolinium Nitrate Hexahydrate [$Gd(NO_3)_3.6H_2O$] /Lanthanum Nitrate Hexahydrate [$La(NO_3)_3.6H_2O$] /Yttrium Nitrate Hexahydrate [$Y(NO_3)_3.6H_2O$] in 30 ml of methanol [CH_3OH] by constant stirring for1 hour at room temperature.

Solution A was added to Solution B drop by drop using addition funnel under continuous stirring. The mixture was then stirred continuously for 2 hours. Gradually, small amount precipitates were formed.

0.04 mole of Sodium sulphide [Na_2S] was dissolved in 30 ml of methanol [CH_3OH] by constant stirring with the help of mechanical stirrer for 30 minutes at room temperature to prepare solution C.

Solution C was added using addition funnel to above mixed Solution drop by drop with continuous stirring. The mixture was stirred continuously for 5 hours at 60 ºC. Gradually, large amount precipitates were formed. The precipitates were filtered and washed with petroleum ether. The filtered precipitates were dried in oven at 50 ºC for 1 hour and allowed to cool.

In order to synthesize 1%, 2% and 3% Mn, Eu and Tb doped Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3, appropriate amount of Nitrates of dopants i.e. Manganese Nitrate [$Mn(NO_3)_2.4H_2O$], Europium Nitrate [$Eu(NO_3)_2.6H_2O$] or Terbium Nitrate [$Tb(NO_3)_2.5H_2O$] were dissolved in 10 ml of methanol [CH_3OH] and the mixture was stirred continuously for 1 hour. This solution was added to the initial solution and the whole procedure was repeated.

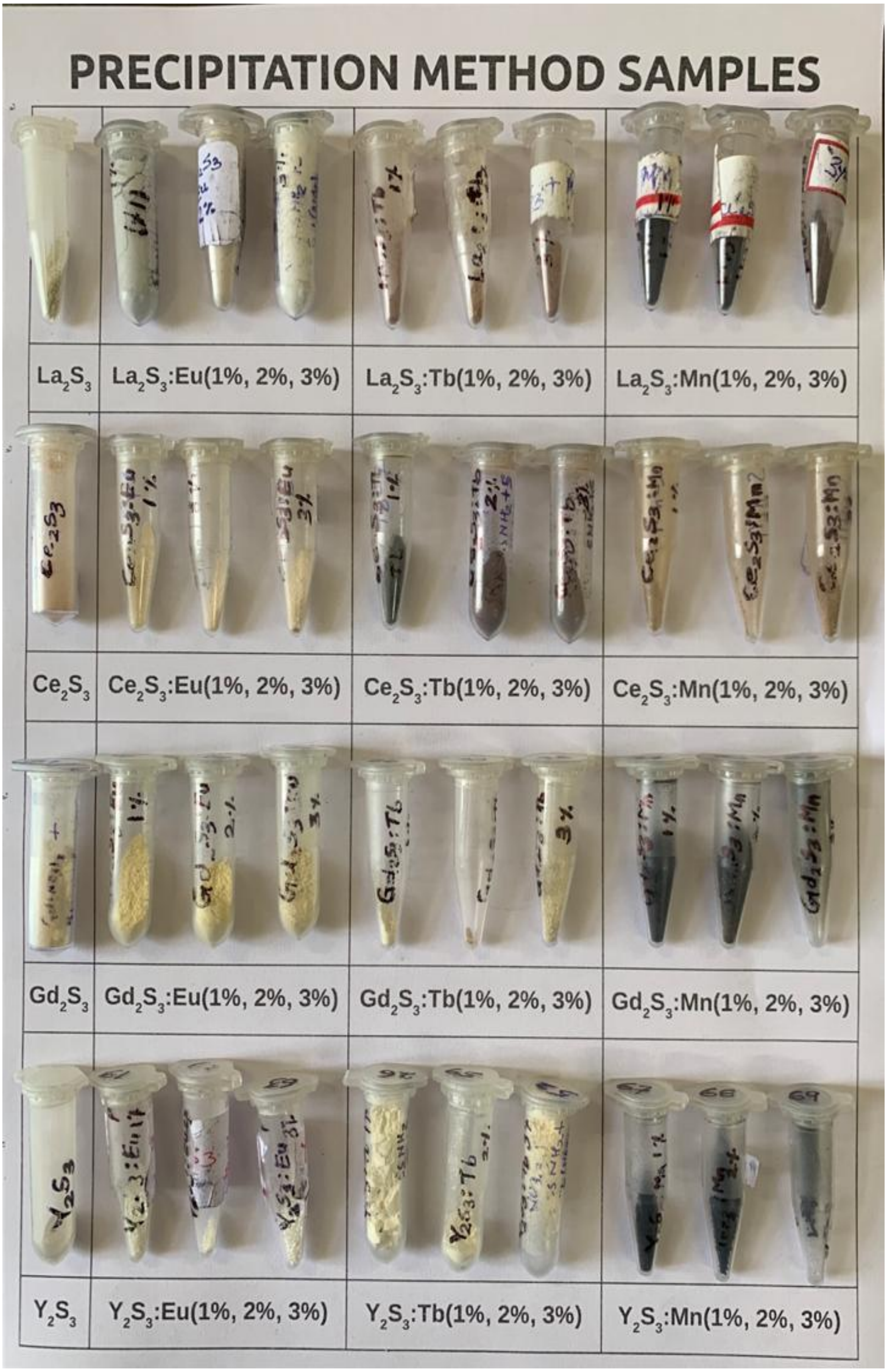


Figure 3-4: Samples synthesized by Precipitation Method

Table 3-2: Coding for samples synthesized by Precipitation Method

Sr. No.	Sample Name	Sample Code
1	Ce_2S_3 Undoped	CeU-P
2	Ce_2S_3 1% Mn Doped	CeM1-P
3	Ce_2S_3 2% Mn Doped	CeM2-P
4	Ce_2S_3 3% Mn Doped	CeM3-P
5	Ce_2S_3 1% Eu Doped	CeE1-P
6	Ce_2S_3 2% Eu Doped	CeE2-P
7	Ce_2S_3 3% Eu Doped	CeE3-P
8	Ce_2S_3 1% Tb Doped	CeT1-P
9	Ce_2S_3 2% Tb Doped	CeT2-P
10	Ce_2S_3 3% Tb Doped	CeT3-P
11	Gd_2S_3 Undoped	GdU-P
12	Gd_2S_3 1% Mn Doped	GdM1-P
13	Gd_2S_3 2% Mn Doped	GdM2-P
14	Gd_2S_3 3% Mn Doped	GdM3-P
15	Gd_2S_3 1% Eu Doped	GdE1-P
16	Gd_2S_3 2% Eu Doped	GdE2-P
17	Gd_2S_3 3% Eu Doped	GdE3-P
18	Gd_2S_3 1% Tb Doped	GdT1-P
19	Gd_2S_3 2% Tb Doped	GdT2-P
20	Gd_2S_3 3% Tb Doped	GdT3-P
21	La_2S_3 Undoped	LaU-P
22	La_2S_3 1% Mn Doped	LaM1-P
23	La_2S_3 2% Mn Doped	LaM2-P
24	La_2S_3 3% Mn Doped	LaM3-P
25	La_2S_3 1% Eu Doped	LaE1-P
26	La_2S_3 2% Eu Doped	LaE2-P
27	La_2S_3 3% Eu Doped	LaE3-P
28	La_2S_3 1% Tb Doped	LaT1-P
29	La_2S_3 2% Tb Doped	LaT2-P
30	La_2S_3 3% Tb Doped	LaT3-P
31	Y_2S_3 Undoped	YU-P
32	Y_2S_3 1% Mn Doped	YM1-P
33	Y_2S_3 2% Mn Doped	YM2-P
34	Y_2S_3 3% Mn Doped	YM3-P
35	Y_2S_3 1% Eu Doped	YE1-P
36	Y_2S_3 2% Eu Doped	YE2-P
37	Y_2S_3 3% Eu Doped	YE3-P
38	Y_2S_3 1% Tb Doped	YT1-P
39	Y_2S_3 2% Tb Doped	YT2-P
40	Y_2S_3 3% Tb Doped	YT3-P

3.4 Characterization Techniques

The characterization techniques used in this study are X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscopy (FE-SEM). The optical properties of the materials were studied using Photoluminescence Spectroscopy (PL) and its thermoelectric properties were studied by calibrating the Resistance → Temperature curve.

Here is a brief mention of the theoretical aspects of the techniques used.

3.4.1 X-Ray Diffraction (XRD)

XRD is a tool used for analyzing the atomic and molecular structure of a crystal. It is used not only for phase identification but also for initial identification of lattice structure. XRD is based on the constructive interference of monochromatic X-Rays from a crystalline sample. The wavelength of X-rays is of the order of the inter-atomic distance and hence get scattered on interaction with a crystalline substance (phase). The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance [6, 7].

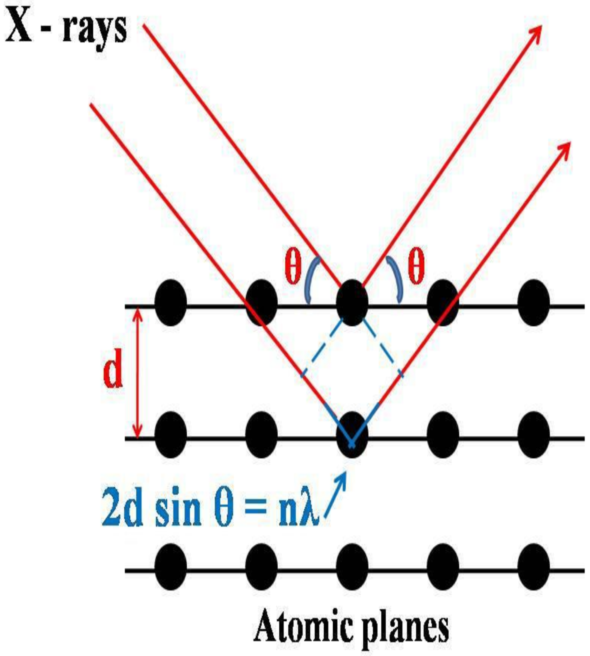


Figure 3-5: Reflection of X-rays by two Successive inter atomic planes

The path difference between the two successive atomic planes with spacing ‘d’ becomes an integral multiple of the wavelength ‘λ’ of the incident radiation at specific angles θ. The relation between these parameters is given by the Bragg’s Equation,

$$n\lambda = 2d \sin\theta$$

where n is an integer, corresponding to the order of diffraction from the crystal planes. The crystal planes act as a grating. Hence, nλ is the path difference between the scattered waves.

The XRD data was analyzed and identification of the phases was carried by comparison with the Joint Committee for Powder Diffraction Standards (JCPDS) files [8].

The crystallite size was estimated by using the Scherer formula [9].

$$\boldsymbol{D = K\lambda\beta\ Cos\ \theta}$$

where D is the crystallite size, K is a constant equal to ~ 0.9, λ is the X ray wavelength, β is the full width at half maximum (FWHM) and θ is the Bragg angle of the peak.

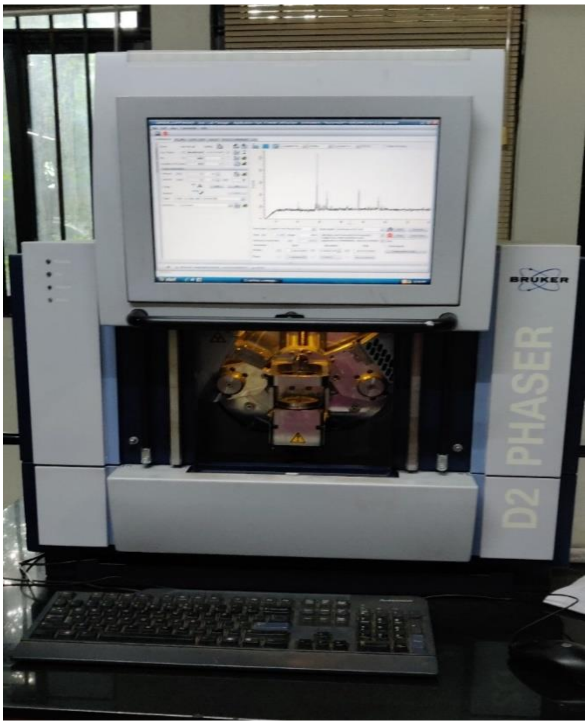


Figure 3-6: Photograph of X-Ray Diffractometer

The XRD patterns in this study were recorded on a D2 Phaser Powder Diffractometer (at the P. D. Patel Institute of Applied Sciences, Charotar University, Changa) with Cu-Kα radiation source (λ = 1.54 Å) operated at 30 kV and 10 mA in the 2Θ range 5 – 80 degree at the scan speed of 0.05 degree per second.

3.4.2 Energy Dispersive X-Ray Analysis (EDAX)

It is desirable to check the chemical composition of the samples after their synthesis. The Energy Dispersive X-Ray Analysis (EDAX) also known as Energy Dispersive X-ray Spectroscopy (EDS or EDX) is an X-Ray technique used for elemental analysis or chemical characterization of the sample.

It works on the basic principle that each element has a unique atomic structure having a unique set of features in its electromagnetic spectrum.

Every atom has a unique number of electrons that belong to certain shells having discrete energies. When an electron beam hits the inner shell of an atom knocking off an electron from the shell, it leaves a positively charged electron hole behind. In order to fill this vacancy, an electron from outer higher energy shell moves to this inner lower energy shell. The difference in energy is released in the form of an X-ray.

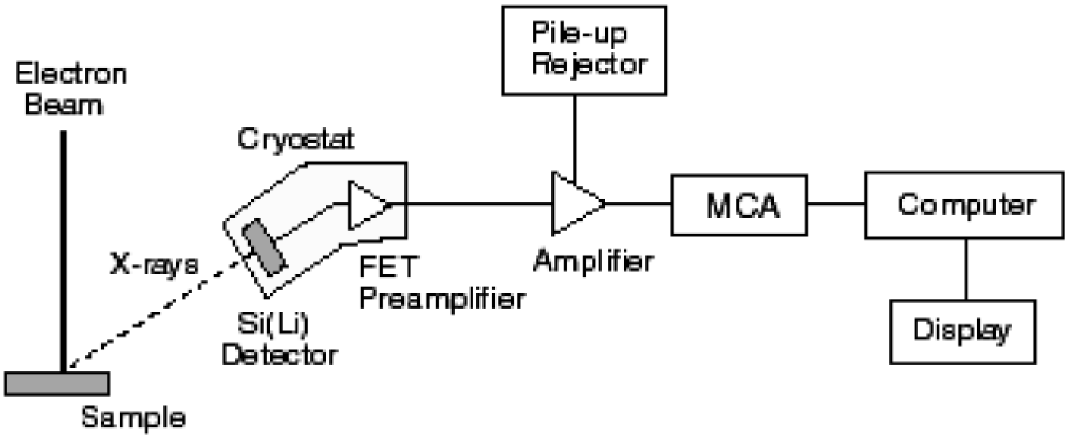


Figure 3-7: Schematic diagram of Energy Dispersive Spectrometer

An EDAX spectrum displays peaks corresponding to the energy levels of these X-rays. Each of these peaks are unique to an atom and hence corresponds to a single element. The higher the peak in the spectrum, the more is its concentration.

The EDAX measurements in this study were done at Sprint Testing Solutions, Mumbai, using the Scanning Electron Microscope mentioned below.

3.4.3 Field Emission Scanning Electron Microscopy (FE-SEM)

The Field Emission Scanning Electron Microscope (FESEM) is an instrument that produces high resolution, three dimensional images which provide topographical and morphological information. The compositional information of the sample can be also obtained as a supplement.

The working principle of FESEM is similar to that of SEM but differs in the way electrons are generated. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode while in FESEM, a field emission gun is used which provides an extremely focused and low energy electron beams.

These primary electrons released from the source provide energy to the atomic electrons of the sample. The interaction between the electron beam and the sample generates X-rays, backscattered electrons, Auger electrons and secondary electrons. All of these provide valuable information about the sample.

The secondary electrons are the only ones which have probability to escape from the surface of the specimen. These electrons are collected from each point of the sample for image construction.

Thus the supplementary output produced on interaction of the electron beam with the sample is given out in several forms, one of them being X-ray, as mentioned above. The energy of this beam is analyzed to get the requisite information about compositional aspects.

Figure 3-8: A Typical Set Up of FESEM

The FESEM measurements in this study were done at Sprint Testing Solutions, Mumbai.

3.4.4 Photoluminescence Spectroscopy (PL)

The optical properties of the synthesized samples were studied using Photoluminescence Spectroscopy (PL). It is based on the principle of generation of light in the visible region of the spectrum after photo excitation. The study is often referred to as fluorimetric analysis and the instrument is called Spectrofluorophotometer.

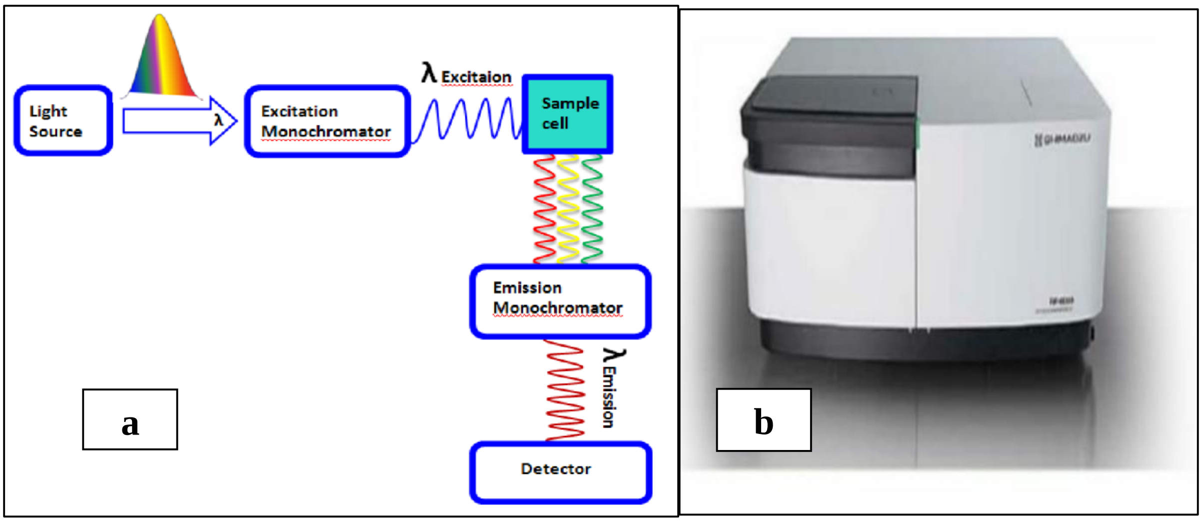


Figure 3-9: (a) A simple view of essential components of Fluorescence Spectrometer (b) A Typical Spectrofluorophotometer

Radiation is directed onto a sample which absorbs it and the electrons temporarily jump to the excited state due to photoexcitation. When electrons return back to the ground state, they release energy having wavelengths in the visible region that can be observed as fluorescent colour.

The fluorescence spectrometer primarily consists of a source of light (150 W Xenon arc-lamp), monochromators, a sample holder and a detector. The monochromators enable the wavelength of incident and emitted radiation to be selectable. The detector signal can be precisely manipulated and presented.

In this study, the PL spectra were recorded with the help of Shimadzu Spectrofluorophotometer (1503R-PC) having 150 W Xe-lamp at room temperature at The Department of Applied Physics, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda.

3.4.5 Thermoelectric Properties

The Thermoelectric properties of the synthesized samples were studied by plotting the Resistance → Temperature curves using Impedance Spectrography which is a highly sensitive technique used to determine the electrical properties of samples.

In impedance spectroscopy measurements, the cell is perturbed with an alternating signal of small magnitude and the way in which the system follows the perturbation at steady state is observed. There are major features associated with this technique, among which the most important are (a) an experimental ability to make high-precision measurements because the response may be indefinitely steady and can therefore be averaged over a long term, (b) an ability to treat the response theoretically by linearized (or otherwise simplified) current-potential characteristics, and (c) measurement over a wide time (or frequency) range.

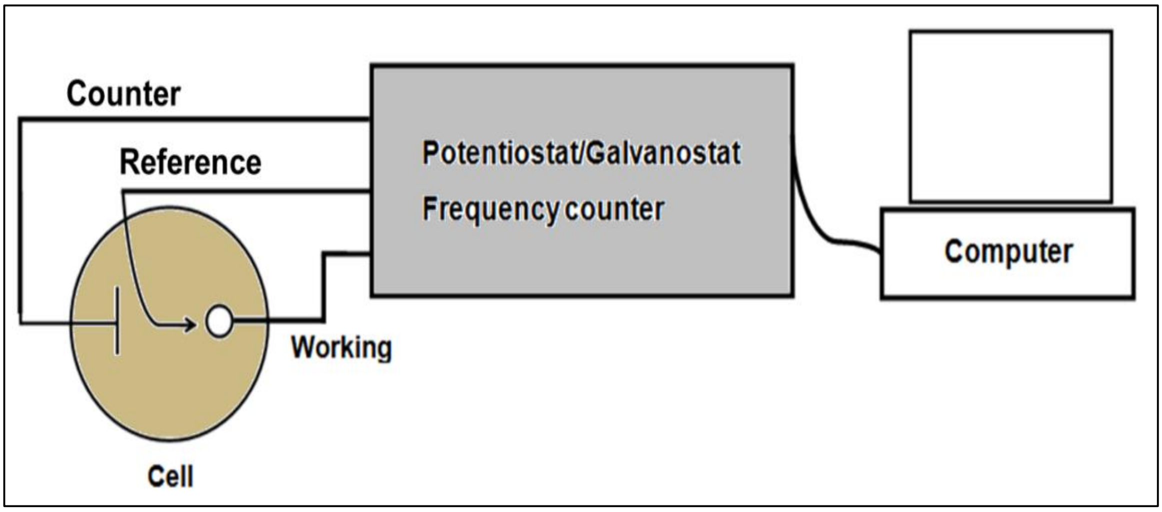


Figure 3-10: A Simple view of the Essential Components of Impedance Spectroscopy

The set up consists of a working, reference and counter electrodes. A known voltage is passed from the working electrode through the sample and into the counter electrode.

In this study a PGSTAT302N potentiostat/galvanostat (Metrohm Autolab) equipped with a FRA2 impedance module and a BOOSTER20A 20A, was used to perform the impedance spectroscopy measurements.

The impedance spectra consisting of Z’ → Z” plots, also known as the Nyquist or Cole-Cole plots were plotted in a complex plane. These plots were converted into the Resistance → Temperature graphs using suitable software.

Figure 3-11: Metrohm Autolab at Pandit Deendayal Petroleum University, Gandhinagar

3.5 Summary

The choice of synthesis method is an important criterion for every research. In this study, the samples have been synthesized using the Solid State Method and the Precipitation Method. Synthesis of Lanthanum Sulphide, Cerium Sulphide, Gadolinium Sulphide and Yttrium Sulphide was carried out with Europium, Terbium and Manganese as dopants. The doping percentages were taken to be 1%, 2% and 3%.

Thus, a total of 80 samples, 40 by Solid State Method and 40 by Precipitation method have been synthesized.

The structure and properties of the synthesized samples were studied using material characterization techniques like X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscopy (FE-SEM). The optical properties of the materials were studied using Photoluminescence Spectrography (PL) and its thermoelectric properties were studied by plotting the Resistance → Temperature curve.

3.6 References

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