Chapter - 2

Experimental Methods and Characterization Techniques

2.1 Introduction

In this chapter, the basic information of hydrothermal, solid state and combustion synthesis methods are explained with their principle, useful parameters, theoretical background and recent scope of the synthesis method in material science and technology. The detailed procedure to prepare phosphors required, materials, sample preparation has been explained in this chapter.

2.2 Experimental Techniques

2.2.1 Synthesis Methods

2.2.1.1 Hydrothermal Method

The hydrothermal word comes from geology formation of nature to establish occurs during the middle of the 19th century. During the investigation of the foundation of some mineral deposits in the Earth's crust and the formation rocks, the geologists had created the simulated information of the hydrothermal conditions of particular locations [1]. On this basis of naturally occurring phenomenon hydrothermal process, this method applied for the development of single crystal growth and powder crystal in various parts of scientific and industrial research from the last two centuries. Using the hydrothermal synthesis process applies to the synthesis of inorganic material through the heterogeneous reactions that take place in the aqueous environment of the reagents formed above ambient temperature and pressure [2, 3]. In this process, an aqueous mixture of reagents prepared from their stoichiometric ratio obtained through the chemical reaction is heated at a constant temperature in an airtight stainless steel shell (autoclave).

The temperature of the autoclave had been raise above the steaming temperature of the water which could be maintained at a constant value < 300°c for 10-24 hours depends on the reaction. However the volume of the autoclave is constant, consequently, the temperature above the boiling point of water increases the pressure within the reaction autoclave which is intensely increased beyond atmospheric pressure [4]. The combined effect of high temperature and pressure in this method provides an extensive single-step chemical process to produce highly crystalline material which could not require post-annealing treatments to obtain pure material. There are several reaction parameters involve in this synthesis method that could immensely affect the property of the synthesized materials such as the type and concentration of the reagents, the solvent, the stabilizing agents, the reaction temperature, and time [5].

In the hydrothermal synthesis method, the development of different types of nanomaterials can be materialized in a wide range of temperatures. The morphology and the crystalline nature of the prepared materials can be controlled by maintaining temperature-pressure conditions in the reaction [6]. Hydrothermal synthesis is the most universally adopted method for the production of materials. Figure 2.1 illustrates the steps followed for the material synthesis through the hydrothermal process.

Perovskites materials are the utmost profuse minerals on the Earth. Generally, Perovskite oxide crystals are anisotropic materials because of their complex structure rather than the ideal crystalline structure which could make its importance in various applications [7, 8]. The hydrothermal synthesis method is the most effective mean for the development of multi-compound oxide or perovskite materials. The characteristics of a sample can be analysed by adjusting reaction conditions like temperature and reactant concentration [9].

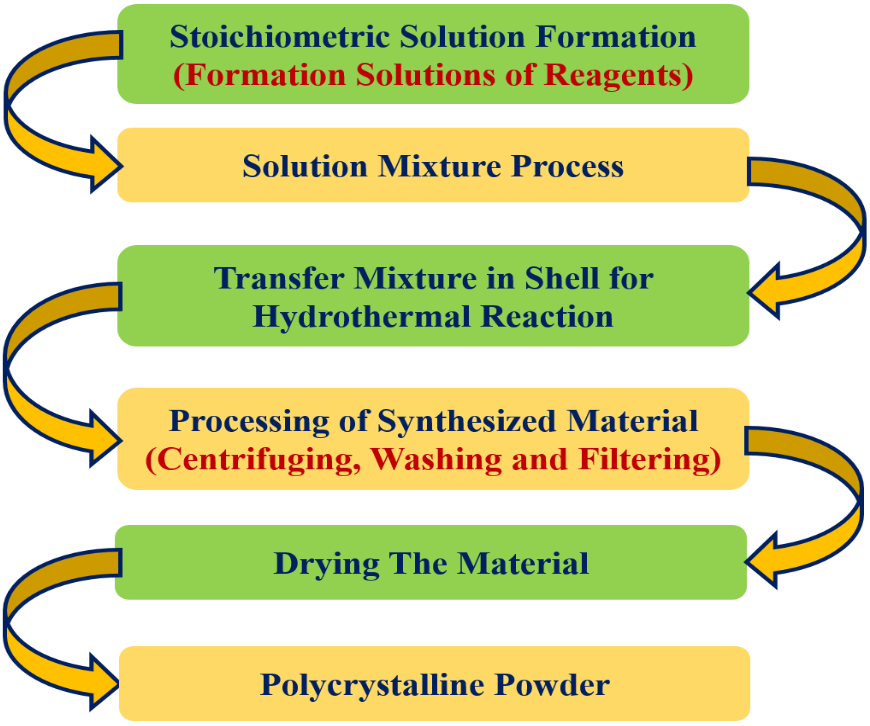

Figure 2.1 Universal steps followed for the material synthesis through hydrothermal process.

Applications of Hydrothermal Synthesis

The hydrothermal processes have been established for the synthesis of wide-range of nanomaterials based on their applications. It has been commonly used for the developing nano materials during recent years for ferroelectricity, piezoelectricity, giant magnetoresistance, information storage, piezoelectric sensors, and luminescent materials [10–13]. Hydrothermal synthesis is an advantageous method to develop bioceramics and biomaterials which is a new class of materials related to organisms or biochemistry. Such materials have extensive medical applications such as artificial bones, joints, and teeth, etc. It has several applications for the preparing thin films, vanadates, garnets, and others [14]. Figure 2.2 shows the various filed of application of hydrothermal synthesis method.

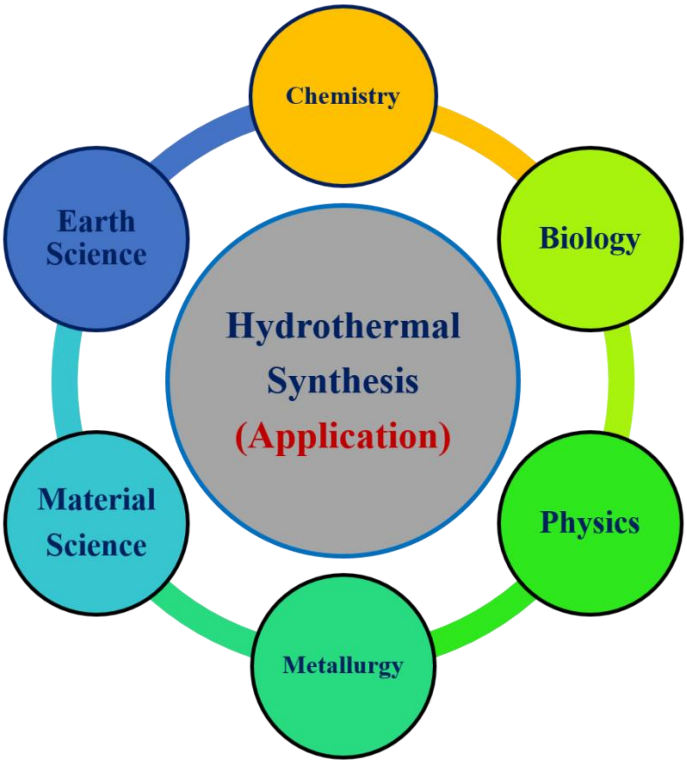

Figure 2.2 Area of application of hydrothermal synthesis method.

Merits and Demerits of Hydrothermal Synthesis

The significant merits of hydrothermal synthesis method over others synthesis methods are listed below. (i) The production of nanomaterials by the hydrothermal method can minimize loss of reagent materials; (ii) The structures of nanomaterials can be easily controlled through the liquid phase chemical reactions; (iii) Various types of nanomaterials with different shape such as nanoparticles, nanorods, nanotubes, hollow nanospheres, and graphene nanosheets have been synthesized using this method; (iv) It is a simple and low cost synthesis method, therefore it is a choice for commercial production of large amount of materials [15, 16]. Demerits of hydrothermal synthesis are listed as (i) This synthesis method require high cost of equipment, i.e. autoclave; (ii) The monitoring of crystal formation process unable up to the end of the synthesis process; (iii) Hydrothermal synthesis can be effected by temperatures and pressures below the critical point and under supercritical conditions for a specific solvent [16, 17].

2.2.1.2 Solid State Reaction

The solid-state synthesis processed through the chemical composition reactions. In this process, a mixture of solid reactant mixed according to the stoichiometric ratio of composite is heated to develop a new solid composite or complex of composite, alloys, ceramic materials and gases, etc. [18, 19] Solid-state reaction route is a generally used to synthesis of polycrystalline material of the order of micrometer from solid reagents. Solid state rout is universally used method for the preparation of composite oxides from simple oxides, carbonates, nitrates, pervoskites, hydroxides, oxalates, and various types of metal alloys [20].

Customarily these procedure involved several annealing treatments compiling with several intermediate grinding processes to increase the homogeneousness as well as to reduce the particle size of the prepared powder materials. In solid state route, usually a very high temperature is employed inside the furnace, in which various factors affect the chemical reaction of reagents and morphological properties. The materials prepared have tuned characteristics such as the reactivity, porosity, surface area, defect levels [21, 22]. The solid-state route is comparatively cheaper method to prepare bulk powder materials at small scale and industrial scale. This process have need of simple arrangement of experimental setup and large scale production of powder is been accomplished in a reasonably simple manner [23, 24]. In this method, the reaction of the reactants used for the preparation of composite occurs without the presence of any catalytic agent at high temperatures. The main advantage of this method is that the final product formed in solid powder which is basically pure with the desired properties [25].

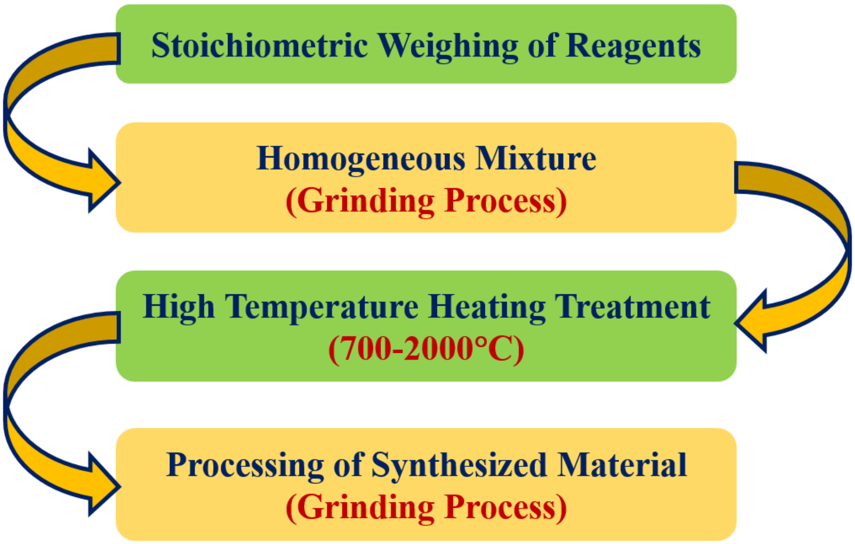

Figure 2.3 Steps for conventional solid state reaction route.

Figure 2.3 shows various steps followed in conventional solid state reaction route. The list of steps followed are; (i) Take suitable high purity reagents according to the stoichiometric chemical reaction balance, reagents used should be in fine grain form. (ii) All require reagents were grinded using agate mortar and pestle to obtain homogeneous mixture. (iii) The mixture was transferred into alumina crucible and placed inside the muffle furnace for the annealing process at high temperature (700-2000°C) for several hours according to type of materials. (iv) After annealing process obtained materials is been grinded to obtain homogeneous polycrystalline powder. Some time to reduce the particle size and homogeneity of material the annealing treatment at different temperature and grinding process are followed for two to three time.

Merits and Demerits of Solid State Reaction Method

The significant merits of solid state reactions method are: (i) It is a cheaper synthesis method as less production of side products during the reaction. In addition to the products do not need any further purification to the remaining solvent and impurities. (ii) In this method, no solvents or any fuel are used in the chemical reaction, therefore no west leftover which is an important factor to develop eco-friendly product. (iii) In this process, the chemical reactions take place faster within a few minutes rather than hours because of the reactants used are in close contact with each other. (iv) It is possible to grow organometallic complexes through solid state method using crystal engineering. (v) Using this method, it is possible to carry out cascade chemical reactions quite easily and with high yields. (vi) The main advantage this method is easily controlling operating conditions [26–28]. Demerits of solid state reactions method are: (i) Generally, the prepared powder is in micrometer size which not a significant property of material in recent area of research. (ii) Some time the reaction produce unwanted toxic gases which is harmful [28].

2.2.1.3 Combustion Synthesis

The word combustion synthesis comes from the materials synthesis through the combustion reactions method which is defined as a rapid oxidation of the oxidants using fuel that generates tremendous amount of heat [29]. In other word, it is a process where the sequence of exothermic chemical reactions takes place between a fuel and an oxidant that produce heat and the conversion of chemical species. Due to its versatile nature, combustion synthesis has been employed in the synthesis of variety of inorganic materials such as oxides, ceramics, pervoskites, metals, and semiconductor composites. In recent times, combustion synthesis is been associated with different scientific subjects connected to the material research such as materials sciences, chemistry and physics. This method gets immense attention in various researcher areas due to its outcome is nanomaterial [29, 30].

The combustion process is carried out through two basic modes: (i) Propagation mode; in this mode, the combustion reaction starts locally by ignition and then spreads to the whole sample with a self-sustained propagation of the combustion wave. (ii) Volume reaction mode; in this mode, the entire sample is uniformly heated to the ignition temperature and the combustion reaction occurs simultaneously in all parts of the sample. It is also called thermal explosion [31–33].

Out of two mode of combustion, the volume reaction mode is most suitable for weakly exothermic combustion reactions in which that preheating of the materials is required prior to ignition. Most of the extensive investigation has been performed on the propagation mode; therefore the fundamental base of combustion synthesis is established on this propagation mode [34, 35]. In this method, the propagation of a combustion wave take place via reaction media i.e. fuel and oxidants used for the combustion. As a consequence, the features of the combustion process and the synthesized material are profoundly dependent on the structure and properties of the reaction media [36, 37].

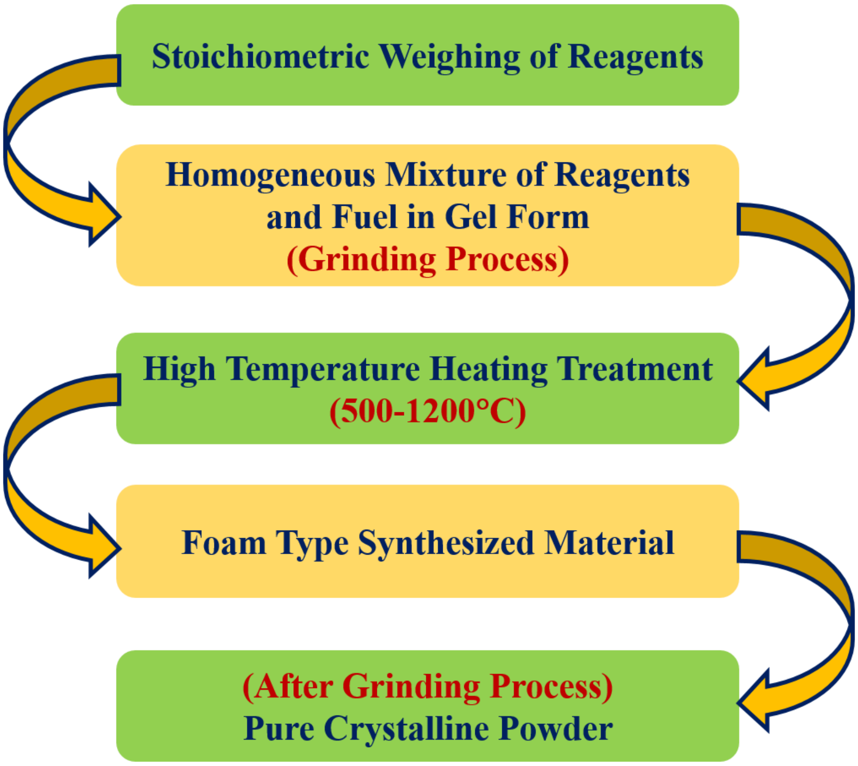

Figure 2.4 Steps for conventional solid state reaction route.

According to the nature of the reaction media, the combustion process can be divided into two categories, namely homogeneous combustion and heterogeneous combustion. In homogeneous combustion, both heat generation and heat transfer are continuous, and the chemical reaction is homogeneous. In heterogeneous combustion, heat generation is discrete and heat transfer is heterogeneous. There are several control parameters which are used to control combustion method to synthesis desired material their diverse applications [38–40]. The calculation of control parameters like nature of flame, temperature variation, nature of atmosphere, chemical compositions of precursor, fuel-oxidant ratio and generated gases, etc. should be organized properly [41]. Combustion synthesis is attractive method for synthesis nanomaterials for a variety of applications such as catalysts, luminescent phosphors, nanomaterials for solid oxide fuel cells, materials for solar cell, and environmental remediation. This method is also utilized for synthesize of many types of complex compound, including binary, pervoskites and other complex oxides [30, 37]. Figure 2.4 shows various steps followed in combustion synthesis.

Merits and demerits of combustion synthesis:

Combustion syntheses have several merits over conventional solid-state reactions: (i) In this method, the heat energy generated by exothermic chemical reactions is used as external heating sources which decreases energy consumption required in reaction. (ii) Cheaper the production of materials due to the easy and low cost equipment is needed in combustion synthesis. (iii) The enormously high temperature is helpful for production of the purity of products by removing unstable impurities by evaporation. (iv) Combustion reactions are rapid process for the development of reactants to products within a very short interval of time. This method has some demerits such as (i) in combustion process of fuel and oxidant occur suddenly at high temperature which further increases the reaction temperature which could be some explosive. (ii) The material synthesis through this method could have multiphase formation due to the nonuniform temperature during the synthesis process which could increase the agglomeration of materials [31, 42].

2.3 Characterization

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is a most resourceful non-destructive technique which make available the element present and the chemical composition of the materials [43]. The synthesized substances or materials are often analysed for the assessment of its crystallinity, phase formation, crystalline size, and the identification of impurity [44]. All kind of materials always produces their characteristic x-ray diffraction pattern, whatever the type of material, it could be crystalline (single or powder), amorphous, liquid or solid, and polymers. This are the basic fact for the firstly characterization of the newly synthesized material by x-ray diffraction technique [45]. Qualitative analysis of the specific constituent material is been accomplished by the identification of the XRD pattern of the substance. In this analysis, the XRD pattern of the prepared material is compared with the reference data (peaks and relative intensities) of the particular class or type of material presented in various international standard data provided by the International Center for Diffraction Data (ICDD) or Joint Committee on Powder Diffraction Standards (JCPDS) [46]. It is possible to analyse XRD data quantitative analysis because the intensities of the diffraction pattern and the position of XRD peak due to single phase of a mixture depend only on the proportion of that phase in the specimen [43].

Instrumentation used for x-ray diffraction

Figure 2.5 Bruker D8 advance x-ray diffractometer.

The x-ray diffraction measurements of synthesized samples have been carried out at UGC-CSR, Indore Center, India. XRD measurements were recorded through the Bruker D8 advance x-ray diffractometer shown in Figure. The diffractometer working on the basis of 1-D position sensitive detector based on silicon drift detector technique which reduces the measurement time significantly without reduction in the diffracted intensity. Cu-Kα is used as x-ray source in Bruker D8 Advance diffractometer. The wavelength of generated x-ray is 0.15406 nm for operating voltage 40 kV and current 40 mA. The XRD measurements were carried out for glancing angle incidence detector at an angle of 2° for 2θ values of 10°–60° in steps of 0.02° s^{-1}.

Applications of XRD

XRD is used to identify the crystalline material, which is exploited during development. It is used for identification of various polymorphic forms from their characteristic fingerprints. It is also used to distinguishing the amorphous and crystalline material. In addition chemical analysis, XRD is widely used for stress measurements and texture analysis. XRD technique can also provide the information about the degree of crystallinity present in polymers. XRD pattern of the material is been used conventionally for bulk sample's analysis as well as thin film analysis. The wavelength of x-ray radiation used in measurement is of the order of the interatomic spacing of crystalline solids, therefore is a very used technique to determine the domain size and the structure of nanomaterials [47, 48].

2.3.2 Fourier Transform Infrared Spectroscopy (FITR)

FTIR spectroscopy is used in various fields of research mainly in material science, biological and chemical sciences to obtain the IR spectrum of the liquid or solid samples in transmission or absorption mode of the spectrometer [49]. FTIR is used to identify the presence of organic and inorganic compounds in the newly synthesized materials. In FTIR spectroscopy, the mathematical tool (i.e. Fourier transform) is used to translate the data recorded through the interferogram into the definite spectrum which represent the particular absorption or transmission band corresponds to the bond formation in material [49, 50]. FTIR spectrometer is mainly used for the range 400–4000 cm^{-1}, where the specific dominating molecular groups present in the sample are determined through IR spectrum. It is also used to determine photoconductivity of solid, liquid, and gas, and the infrared spectrum of absorption and emission of the materials. All type organic, inorganic, and polymeric materials are analyzed using FTIR spectroscopy [51, 52]. Any modifications occur in the characteristic IR spectral pattern of absorption or transmission bands evidently indicate the change in the formation of material composition. It is very useful technique for the identification of unknown materials, discovering contaminants present inside the material, finding impurity, and detecting decomposition and oxidation of the material [53, 54].

Working of FTIR Spectrometer

Figure 2.6 shows the schematic diagram of working of Michelson FT-IR Spectrometer. Modern FTIR spectrometers is been developed to perform high quality Fourier Transform Infrared Spectroscopy (FT-IR). The working of modern FTIR spectrometer is based on Michelson Interferometer. The purpose of Michelson interferometer in modern spectrometer is that, it allows all the frequencies to reach the detector at once and not one at the time which is useful to obtain all information about the material for all IR frequency. When a beam of IR radiation containing wide range of frequency is incident on a sample material, selected frequencies of the IR radiation is absorbed by the sample according to its characteristic while remaining frequencies pass or transmitted through it. The transmitted frequency of the resulting signal are detect at the detector which is represent the transmitted IR spectrum of the molecular formation called 'fingerprint' of the material. The important practicality of the FTIR spectroscopy ascends because different materials have different chemical structures and bond formation that produce diverse spectral fingerprints. The IR spectral characteristics of the materials synthesized with different synthesis technique could be different due to the structural change occurs due to synthesis process [55, 56].

The components of Michelson FT-IR Spectrometer are listed below:

1. Light source
2. He-Ne gas laser
3. Beam splitter (half silvered mirror)
4. Translating (movable mirror)
5. Optical System (fixed mirror)
6. Sample chamber
5. Detector and Computational set up

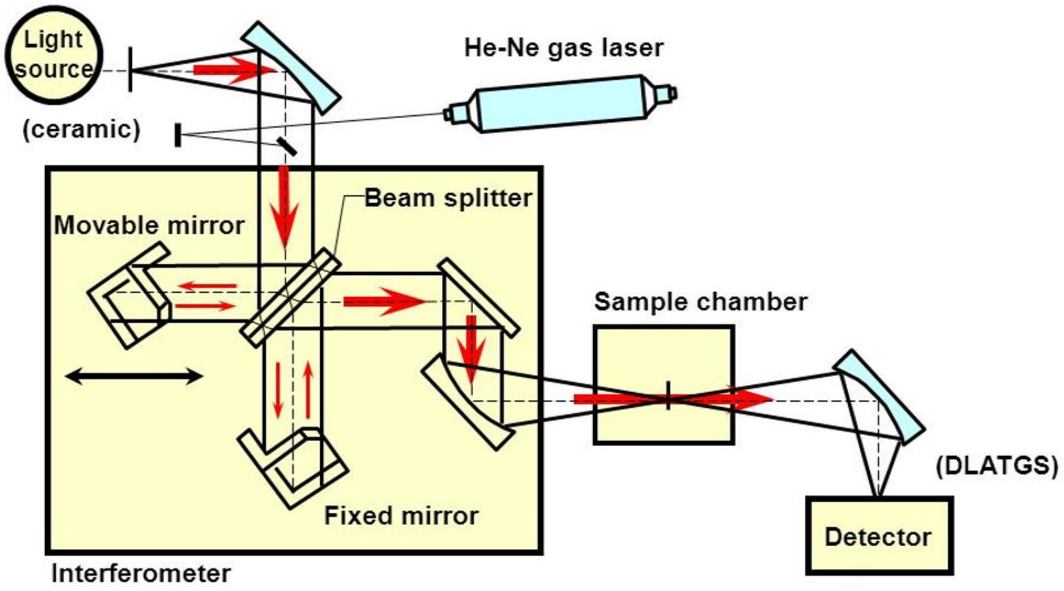

Figure 2.6 Working of modern FTIR spectrometer.

Instrument used for FTIR

FTIR measurements of all synthesized samples have been done at Department of Physics, The M. S. University of Baroda, Vadodara. FTIR spectra were recorded through the JASCO – 4600 Fourier Transform Infra-Red spectrometer shown in Figure 2.7. Fourier transform infrared (FTIR) spectra of the samples were recorded by FTIR-4100 type A IR spectrometer in transmittance mode in wavenumber range of 400–4000 cm^{-1}.

Figure 2.7 JASCO – 4600 Fourier Transform Infra-Red spectrometer**.**

Application

FTIR is a fundamental analytical tool to in various fields. In chemical, physical and pharmaceutical research, it is used for the identification of newly developed materials or drugs. In forensic investigation, it is used to scrutinize specimens, to detect the existence of targeted composites and to measure the amounts of the composites present in the sample. In polymer industry, it is used to investigate the phases of the plastic and polymer product. It is also used in the identification of lifecycle of polymers, quality control, and reverse engineering, etc. FTIR is widely used food research, environment and water quality analysis, biochemical, biomedical research, coating and surfactant analysis, textile research, etc [55, 57–59].

2.3.3 SEM (Scanning Electron Microscopy)

History

The development of a SEM began a few years after the invention of a TEM by Ruska in 1931. But the commercialization of SEM required about 30 years. The history of the initial development stages of SEM are as follows;

- Invention of TEM by E. Ruska in 1931.
- Original SEM prototype by M. Knoll in 1935.
- SEM (STEM) with lens system by M. von Ardenne in 1938.
- SEM for bulk specimen observation by V.A. Zworykin in 1942.
- Basic research and development of application technologies at Oatley Lab in duration of 1945-1960.
- Commercialization of SEM in 1965.

In 1965, Cambridge Scientific Instruments (UK) and JEOL (Japan) first commercialized a SEM, individually. During the four decades after the first commercialization of the SEM, about several tens of thousands of SEMs have been manufactured.

Basic Information of SEM

The discovery of electron microscopes is happened due to the constraints of light microscopes. Light microscopes have limitations to magnify the objects up to the range of visible light [60, 61]. As the dimensions of the particle size of material science and other scientific exercises are limited to the order of micro to nano size, it is not possible to examine characteristic structures by light microscopy. Scanning Electron Microscope (SEM) is an instrument that can use a high energy electron beam to scan an object with a fine-scale of the order of micro to nanoscale [62, 63]. The scanning of material can provide information about the topography, morphology, composition, and crystallography of the object, and other qualities such as electrical conductivity. SEM is essentially used to examine the surfaces of objects [64].

Principle

In SEM, a high energy electron beam incident on the substance that can originate secondary electron according to the structure and morphology of the material [63, 65]. These secondary electrons collected by the positively charged detector placed at high potential. The scintillation effect on the photomultiplier tube is generated by secondary electrons. These scintillation effects are further converted into electrical signals. The signals are then changed by the video amplifier which converted into 3-dimensional image of the sample by the system. In SEM, the picture is forming due to the synergy of the incident electron with the material that produces various signals, which can be used to obtain information about the surface topography and composition [64, 66].

Working of SEM

The main SEM components include:

- Source of electrons
- Column down which electrons travel with electromagnetic lenses
- Electron detector
- Sample chamber
- Computer and display to view the images

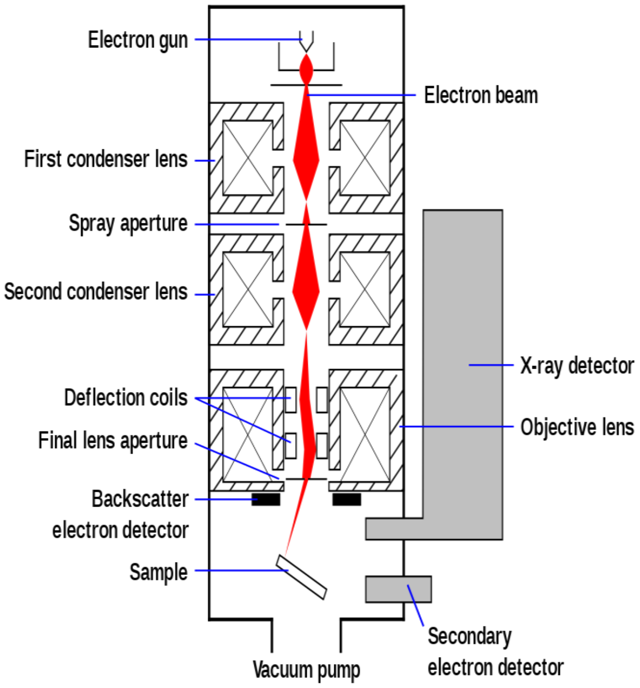

Figure 2.8 Schematic diagram of Scanning Electron Microscope

Figure 2.8 show schematic diagrams of SEM. Electrons are produced at the top of the column, accelerated down and passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample. The sample is mounted on a stage in the chamber area and, unless the microscope is designed to operate at low vacuums, both the column and the chamber are evacuated by a combination of pumps. The level of the vacuum will depend on the design of the microscope.

The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam restoring or scanning, as the name of the microscope suggests, enables information about a defined area on the sample to be collected. As a result of the electron-sample interaction, a number of signals are produced. These signals are then detected by appropriate detectors.

Instrument used for SEM

SEM measurements of the synthesized sample have been done through the Scanning Electron Microscope (SEM) “JSM-7500F” shown in Figure 2.9. The “JSM-7500F” (SEM) has specialties of an optical system that includes a semi-in-lens type objective lens, which can use to collimate the electron beam even at low accelerating voltages. The overall purpose of the JSM-7500F SEM system is to deliver a high-resolution image of the specimens.

Figure 2.9 “JSM-7500F” field emission scanning electron microscope (SEM).

Uses of SEM

SEM has a wide range of application in fields of various branches of science and engineering that allowing researchers working on a wide range of projects in the different fields to access useful information about microscopic processes take place in their research with macroscopic inferences. SEM is widely used to examine the surface topographies of the object or materials, the morphology of the materials like shape and size of the particles. SEM is also used to examine composition of the materials like the different elements and compounds that the object content, and the relative percentage of amounts of elements, crystallographic information such as the structure of particle (nanoscience) and porosity of the material, etc [67, 68].

2.3.4 Photoluminescence

Luminescence is the phenomenon in which electronic states of solid are excited by some energy sources (Infrared, ultraviolet, visible light for PL and heating in TL), and excitation energy is re-emitted as a light of longer wavelength (Stokes Law). Light is traveled onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. In the case of photo-excitation, this luminescence is called photoluminescence [69]. Photo-excitation originates electrons within a material to move into allowable excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process) [70]. The emitted light (photoluminescence) energy relates to the variation in energy levels between the two-electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials.

Instrument Used for Photoluminescence

Figure 2.10 Spectrofluorometer Shimadzu RF-5301 for PL measurement.

The photoluminescence (PL) of all the samples were investigated on a Shimadzu spectrofluorophotometer (model: **RF5301 PC**; **Shimadzu** Japan) at room temperature with Xenon lamp as excitation source at Applied Physics Department, M.S.University of Baroda.

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