Chapter III Experimental techniques and Synthesis of La$_{1-x}$Sr$_x$MnO$_3$

3.1 Introduction

The sample characterization is an important step in the progress of superior materials. The complete characterization of any material consists of phase analysis, compositional analysis, structural analysis, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. In this chapter different analytical instrumental techniques used to characterize our samples are described with principles of their operation and working. The samples were characterized by various experimental techniques in this work such as

1. Thermogravimetric-Differential Thermal Analysis (TG-DTA)
2. X-ray diffraction technique (XRD)
3. Scanning Electron Microscopy (SEM)
4. Energy dispersive X-ray analysis (EDAX)
5. Transmission Electron Microscopy (TEM)
6. Fourier Transform Infrared Spectroscopy (FTIR)
7. Dielectric measurement system
8. Vibrating Sample Magnetometer (VSM)
9. Superconducting Quantum Interference Device (SQUID)

The present chapter gives a brief account of the theory and principle of various experimental techniques used for the current study followed by solution combustion synthesis of La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) samples. All the LSMO samples were characterized by XRD, SEM, TEM and EDAX and FTIR.

3.2 Experimental techniques

3.2.1 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

Thermal analysis is used for the measurement of physical or chemical changes of the materials as a function of temperature, usually heating or cooling at a uniform rate. There are two types of thermal analysis
(i) Thermogravimetric analysis: Measures weight loss or gain during programmed heating of sample

(ii) Differential thermal analysis: Measures temperature difference (ΔT) between a sample and reference material during heating.

**Thermogravimetric Analysis (TGA)**

Thermogravimetry is a technique by which the weight of a substance, in an environment heated or cooled at controlled rates to record as a function of time and temperature. It indicates that the basic requirement is method of heating (or cooling) by means of weighing. There are three types of thermogravimetry,

a. **Isothermally or static thermogravimetry:**
   The sample weight is recorded as a function of time at constant temperature.

b. **Quasi static thermogravimetry:**
   The sample is heated to constant weight at each of the series of increasing temperatures.

c. **Dynamic thermogravimetry:**
   The sample is heated in an environment where temperature changes in predetermined manner, generally at linear rate and weight changes in the sample are recorded. In present work, dynamic thermogravimetry is used.

**Recording of data**

The instrument for thermogravimetry is a precision balanced programmed for a linear rise of temperature and it acts as a thermo balance.

A plot of weight change Vs temperature or time shows results from the programmed operation of thermo balance. This plot is referred as the thermogravimetric curve or TG curve.
The weight change should be plotted on the ordinate with weight decreasing downwards and temperature \((T)\) or time \((t)\) on the abscissa increasing from left to right. Typical TG curve is shown in the Figure 3.1.

![Typical TG Curve](image)

**Figure 3.1** Typical TG Curve

**Information from TG curve:**

The following features at the TG curve should be noted.

1. The horizontal portion indicates that there is no weight change. It reveals, the thermal stability of the material. The ability of the substance to maintain its properties, nearly unchanged as possible on heating (region \(AA'\)) which gives information about the thermal stability. The TG curve is important to the engineers for the preparation of phase pure oxide material. Also, it reveals the temperature range over which substance like alloys; polymers and high pressure values may be safely used.

2. The curve portion \(A'B'\) indicates weight loss in the material.

3. The TG curve gives information about how much weight is lost by heating a sample to given temperature.
4. From the TG curve, the actual decomposition temperature can be determined. This is indicated by \( T_i \) as shown in Figure 3.1. The thermo balance can detect the actual decomposition temperature at which the cumulative mass change reaches a certain value.

5. Final temperature is a temperature at which the cumulative weight change reaches its maximum value corresponding to the complete reactions. It is indicated by \( T_f \) on a TG curve.

6. The reaction interval is the difference between the \( T_f \) and \( T_i \).

The curve is useful for quantitative analysis of substances which undergo loss of volatile components at temperature below 1200 °C. Quantitative analysis is done by measurements from the thermal curve.

The mass loss (m) obtained during a process in which a known molecular weight component is vaporized form the sample. The mass loss obtained from the vertical distance on the thermal curve between the horizontal partitions prior to and after the mass loss.

**Differential thermal analysis (DTA)**

The DTA technique is simple as it involves the recording of difference in temperature between a substance and a reference material against either time or temperature. As the two specimens are subjected to identical temperature regimes in an environment heated or cooled at controlled rate. Thus differential thermo grams consist of record of the difference in sample and reference (\( T_r \)). An ideal DTA consist of an exothermic peak and endothermic peak both the shape and size of the peak may furnished good information about the nature of test samples. Generally, sharp endothermic peak gives idea of change in crystallinity or fusion process where as broad endothermic signifies dehydration reaction in most of the cases. The physical changes give the rise to endothermic curves where as chemical reaction give rise to exothermic peaks. The region of temperature difference in the sample lies in the energy difference between the products and the reactants or
between the two phases of substance. This energy substance is manifested as an enthalpy changes either exothermic or endothermic.

The DTA curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample reaches the temperature of the change of state, the additional heat flux reaching the sample will not increase the sample temperature at same rate as that of the reference and the differential signal appears as a peak. The differential signal would return to the base line only after the change of state of sample is completed and the temperature becomes equal to the reference material.

**Specifications:** It is SDT-2960 from TA Instruments, USA. It is capable of performing both differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) at the same time. Differential Thermal Analysis (DTA) can also be carried out using SDT 2960. This SDT-2960 controller is connected to PC and the special software makes the thermal analysis. It stores the data as well as runs the analysis programs [1].

3.2.2 X-ray Diffraction technique (XRD)

The x-ray diffraction is used as basic characterization technique for different materials. This technique has emerged as powerful tool for determining the crystal structure [2] chemical analysis, stress measurements, phase equilibria and particle size. The XRD pattern is the finger print of a crystalline material [3] as this technique gives information on the structure, phase and purity of a material.

The basic principles of X-ray diffraction are found in classic textbooks e.g. by Buerger [4], Klug and Alexander [5], Cullity [6], Tayler [7], Guinier [8], Barrett and Massalski [9].

Figure 3.2 shows the schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is of the same
order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg’s law and is given as,

\[ 2d \sin \theta = n \lambda \] ...... (3.1)

where,

\[ d = \text{interplaner spacing} \]
\[ \theta = \text{diffraction angle} \]
\[ \lambda = \text{wavelength of x-ray} \]
\[ n = \text{order of diffraction} \]

In crystalline solids the atoms are ordered in particular repeated pattern referred as unit cell with its interatomic spacing comparable to wave length of x-rays (0.5 to 2.5Å). Hence crystals are the best gratings for the diffraction of x-rays. The directions of diffracted x-rays give information about the atomic arrangements and hence the crystal structure and phase formation can be confirmed by x-ray diffraction studies.

![Schematics of x-ray diffractometer.](image)

**Figure 3.2** Schematics of x-ray diffractometer.
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The way of satisfying Bragg’s condition is devised and this can be done by continuously varying either $\lambda$ or $\theta$ during the experiment. The way, in which these quantities are varied, distinguish the three main diffraction methods and tabulated in Table 3.1.

Table 3.1 X-ray diffraction methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\lambda$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laue Method</td>
<td>Variable</td>
<td>Fixed</td>
</tr>
<tr>
<td>Rotating crystal</td>
<td>Fixed</td>
<td>Variable (in part)</td>
</tr>
<tr>
<td>Powder Method</td>
<td>Fixed</td>
<td>Variable</td>
</tr>
</tbody>
</table>

In powder method the crystal to be examined is reduced to a fine powder and placed in a beam of a monochromatic x-rays. Each particle of the powder is the tiny crystal, or assemblage of smaller crystals, oriented at random with respect to incident beam. Some of the crystals will be correctly oriented so that their (100) planes, for example, can reflect the incident beam. Other crystals will be correctly oriented for (110) reflections and so on. The result is that every set of lattice planes will be capable of reflection. This is the principle of a powder diffractometer.

Ideally, according to Bragg’s law, for the particular $d$ value, the constructive interference of x-rays should occur only at particular $\theta$ value i.e Bragg’s angle and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum there.

**Identification of Phases:** From the $d$-spacing, phases can be identified in a sample using the standard JCPDS powder diffraction file and the reflections can be indexed with Miller indices.

However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at $\theta \pm d\theta$, which broadens the peak
corresponding to diffracted beam in proportion to the size of the tiny crystal. This can be used to calculate the particle size. The relation for the same is given by Debye Scherrer’s and formulated as,

\[ t = \frac{0.9\lambda}{\beta \cos \theta} \]  

where, \( t \) = particle size, \( \theta \) = diffraction angle, \( \lambda \) =wavelength of X-rays and \( \beta \) line broadening at Full Width at Half Maxima (FWHM).

**Specifications:**

Model: PW 3710/ PW1710 PHILIPS, Holland

Angle (2\( \theta \)): 10° to 100°

Target: Cu.

Normal mode: PW3710/PW 1710 APD Controller.

3.2.3 Scanning Electron Microscopy (SEM)

The primary use of SEM is to study the surface topography and morphology of solids. Any solid material may be studied by this technique. Scanning electron microscope (SEM) is an instrument that is used to observe the morphology of the sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope [10]. Basically SEM is used for topographical and compositional observations of surfaces, elements analysis of specimen, internal structure, internal characteristics, crystalline structure and magnetic domain observations.

The interaction of electrons with elements is well understood and has been extensively used for characterizing of the materials. When the electrons can be focused to micron or sub-micron size, it is well suited for analyzing sub-micron sized areas. When an electron strikes the atom, variety of interaction products are evolved. Figure 3.3 illustrates these various products and their use to obtain the various kinds of information about the sample. Scattering of
electron from the electrons of the atom results into production of backscattered electrons and secondary electrons. Electron may get transmitted through the sample if it is thin. Primary electrons with sufficient energy may knock out the electron from the inner shells of atom and the excited atom may relax with the liberation of Auger electrons or X-ray photons. All these interactions carry information about the sample. Scanning electron microscope is an instrument that uses electron beams to observe the morphology of a sample at higher magnification, higher resolution and depth of focus. Of these, backscattered electrons, secondary electrons and transmitted electrons give information about the microstructure of the sample. Auger electron, ejected electrons and X-rays are energies specific to the element from which they are coming. These characteristic signals give information about the chemical identification and composition of the sample.

A well focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM application, their intensity being dependent on the atomic number of the host atoms. Each may be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube. To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the C.R.T. beam in synchronization with this.

The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor C.R.T. screen. Change in brightness represents change of a particular property within the scanned area of the specimen [11]. The ray diagram of scanning electron microscope is shown in Figure 3.4.

The scattering cross section for back-scattered electrons is given as [16],
\[ Q = 16.2 \times 10^{-30} \left( \frac{Z}{E} \right)^2 \cot \left( \frac{\phi}{2} \right) \] ...... (3.3)

where, \( Z \) is atomic number and \( E \) is electric field.

Here the cross-section is proportional to \( Z^2 \). Hence, the back-scattered electrons are used for the \( Z \) contrast or for compositional mapping.

Requirements for scanning electron microscopy and typical operating parameters are as follows.

- **Vacuum**: Electrons, being charged particles, require vacuum environment for transversing without change in their number and density.
- **Samples**: Samples being analyzed need to be electrically conducting, otherwise there will be charge buildup due to impinging electrons which gives rise to jumping of the beam and hence its instability.

Thus, in conclusion sample must be vacuum compatible and electrically conducting.

**Specifications:**

- **Model**: JEOL, Japan make JSM- 6360 (HV).
- **Resolution**: 3 nm.
- **Acceleration voltage**: 0.5KV to 30 KV
- **Maximum magnification**: upto X 3,00,000 is possible.
Figure 3.3 Variety of interaction products evolved due to interaction of electron beam and sample.

3.2.4 Energy dispersive x-ray Spectroscopy (EDAX)

The characteristic x-rays can be used for elemental detection and quantization for compositional analysis. There are two techniques are used for analyzing x-ray spectrum.

1. Wavelength dispersive x-ray analysis (WDAX) or (WDS)
2. Energy dispersive x-ray analysis (EDAX) or EDS

These techniques deal with diffraction of x-rays under analysis and can be termed as wavelength (or energy) dispersive spectroscopy also.

- Wavelength dispersive x-ray analysis (WDAX) or (WDS)

The characteristics x-ray are identified by their wavelengths by diffracting them on a crystal monochromator of known ‘d’ spacing and
following Bragg’s law, \( n\lambda = 2dsin\theta \). In fully focusing spectrometer sample, crystal and detector all lies on the same circle called as Rowland circle such that Brag’s law satisfied in all cases. The crystal moves on a linear path in order to maintain constant take off angle. The centre of Rowland circle moves on arc with x-ray source as centre.

- **Energy dispersive X-ray analysis (EDAX) or (EDS)**

  Here, the characteristics X-rays are identified by their energy using solid state detectors. It consists of semiconductor Si(Li) counter and FET amplifier, both cooled by liquid nitrogen and multichannel analyzer (MCA). The utility of this kind of spectrometer is based on two properties

  1. The excellent energy resolution of Si(Li) counter.
  2. The ability of MCA to perform rapid pulse height analysis.

  Semiconductor counter produces pulses proportional to the absorbed energy with better energy resolution than any other counter. The silicon and germanium are the best detectors for X-rays and \( \gamma \)-rays respectively. The pure silicon in intrinsic semiconductor has very high electrical resistivity especially at low temperatures [12].

  Hence, only few electrons are thermally excited across the energy gap into conduction band. However, incident x-ray can cause excitation and thereby create a free electron in the conduction band and free hole in the valance band. If high voltage is maintained across opposite faces of the silicon crystal, the electrons and holes will be swept to these faces, creating small pulse in the external circuit. The schematic diagram of EDS detector is shown in Figure 3.5.
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Figure 3.4 Ray diagram of Scanning Electron Microscope

Figure 3.5 Schematic of EDS detector
It is very difficult to get pure silicon. Hence a p-type Si, lightly doped with boron, were used and to make it intrinsic this is again doped with Li. Typically the resolution of Si(Li) detector is given as 147 eV for manganese Ka radiation of 5.9 KeV energy. The energy dispersive system can analyze whole x-ray spectrum simultaneously. Due to low ionization potential of Si(Li) the count rate is very high (>10,000 c/s/nA) and hence very low current is required. It is used in combination with SEM where current used is very low (of the order of pA).

3.2.5 Transmission Electron Microscopy

The transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or a layer of photographic film, or to be detected by a CCD camera. Virtually, TEM is useful for determining size, shape and arrangement of the particles which make up the specimen. Transmission electron microscopy (TEM) is typically used for high resolution imaging of thin films of a solid sample for nano structural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high energy electron beam, which is diffracted by the lattices of crystalline or semicrystalline material and propagates along different directions, (ii) imaging and angular distribution analysis of the forward-scattered electrons (unlike SEM where back scattered electrons are detected), and (iii) energy analysis of the emitted X-rays. The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of mesoporous materials, viz., hexagonal, cubic or lamellar [13]. TEM also provides real space image on the atomic distribution in the bulk and surface of a nanocrystal [14].

TEM operates on principles similar to that of the optical microscope [15, 16]. The sample illumination source in a TEM is a beam of electrons. This beam of electrons travels through a column under vacuum and is then focused into a very narrow beam with electromagnetic lenses. Some electrons will scatter
and those that do not scatter strike a fluorescent screen giving rise to a contrast image based on sample density. Since the limit of resolution is in the order of a few angstroms, it is a very useful and powerful tool for nanoparticles characterization. Low resolution TEM can generally provide information regarding the size and overall shape of the sample and is routinely used to elucidate such information.

The ray diagram of TEM is shown in Figure 3.6. The accelerated ray of electrons passes a drill-hole at the bottom of the anode. The lens-systems consist of electronic coils generating an electromagnetic field. The ray is first focused by a condenser. It then passes through the object, where it is partially deflected. The degree of deflection depends on the electron density of the object. The greater the mass of the atoms, the greater is the degree of deflection. After passing the object the scattered electrons are collected by an objective. Thereby an image is formed, that is subsequently enlarged by an additional lens-system (called projective with electron microscopes). Thus the formed image is made visible on a fluorescent screen or it is documented on photographic material. Photos taken with electron microscopes are always black and white.

### 3.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

A variety of IR techniques have been used in order to get information on the surface chemistry of different solids. With respect to the characterization of metal oxides two techniques largely used, namely the transmission/absorption and the diffuse reflection techniques. The infrared spectroscopy is the method of qualitative analysis of organic material and it has broad application in inorganic substances as well. The molecular vibrations in the sample can be detected by the vibration spectroscopy. The roots of the vibrational spectrometry are strengthened by the discovery of inelastic scattering of the photons also known as "Raman effect" in 1928 by Raman and Krishnan [17].
It is well known that, IR encompasses a spectral region from red end of visible spectrum (12,500 cm\(^{-1}\), 0.8 mm) to the microwave 10 cm\(^{-1}\), 1000 mm) in the electromagnetic spectrum.

![Figure 3.6 Ray diagram of Transmission Electron Microscope](image)

**Figure 3.6 Ray diagram of Transmission Electron Microscope**

However, based upon applications and instrumentation involved, it is divided in to near (12,500 to 4000 cm\(^{-1}\)), mid-IR (4000 to 400 cm\(^{-1}\)) and far-IR (400 to 10 cm\(^{-1}\)). It is found that most of the fundamental molecular vibrations occur in mid-IR region. Modern Fourier transform IR spectrometers are superior to that of dispersive IR spectrometers on several counts. Due to these advantages the measurements of transmission, reflection or even emission spectra has become significantly faster and even with higher sensitivity than ever before. FTIR spectrometers are based upon Michelson interferometer. Figure 3.7 shows schematic of the spectrometer. A typical spectrometer
mainly consists of components like (a) radiation source, which is always Nernst filament (ZrO$_2$ + Y$_2$O$_3$) or Globar (SiC), (b) optical path and monochromator, in which the beam is guided and focused by the mirrors aluminized or silverized on their surfaces. (c) detectors, which detects the heat radiations.

Figure 3.7 Block diagram of the FTIR

To obtain an IR absorption spectrum, one mirror of the interferometer moves to generate interference in the radiations reaching the detector. However as all wavelengths are passing through the interferometer, interferogram is a complex pattern. In these experiments the absorption/transmission spectrum as function of wavenumber (cm$^{-1}$) is obtained from the Fourier transform of the interferogram, which is the function of the mirror movement. Interestingly, this design doesn't have the reference cell which is generally used in the dispersive IR instrument, so a reference spectrum is recorded and stored in the memory to subtract from the sample spectrum.
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**Instrument Specifications**

Model: PERKIN ELMER SPECTRUM 100  
Range: 400 – 4000 cm$^{-1}$

**3.2.7 Dielectric measurement system**

The dielectric measurement system is a general purpose LCR meter for inspection of component, quality control and laboratory use. The HP 4284A is used for evaluating the component and semiconducting devices over a wide range of frequency of 20Hz to 1MHz and test signal levels (5mV to 2Vrms, 50µA to 20mA rms). It offers the C-D measurements with a basic accuracy of ±0.05% (C), ±0.005 (D) at all test frequencies with six digit resolution (The dissipation factor resolution is 0.000001) on every range [18].

With it’s built in comparator, the HP 4284A can output comparison/decision results for sorting component. By using the handler interface and scanner interface options, the HP 4284A can easily combined with a computer, scanner and fully automate component testing, sorting and quality control data processing. The HP 4284A list of sweep function permits entry of upto ten, frequency test signal levels or bias level point to be automatically measured. The HP-IB interface is a standard interface on HP 4284A and can be used to build an automate test signal to completely new component of material.

It measures two component of the complex impedance at the same time in a measurement. The measurement parameters are listed below

**A) Primary parameters**

1. $|Z|$ Absolute value of impedance  
2. $|Y|$ Absolute value of admittance  
3. L Inductance  
4. C Capacitance  
5. R Resistance

**B) Secondary parameters**

1. D- Dissipation factor
2. Q-Quality factor
3. Rs-ESR (Equivalent Series Resistance)

**Specification:**

1. Model: HP 4284A
2. Power: 220VAC ±10 %
3. Frequency of AC: 47 to 66 Hz

![Image of a dielectric measurement system](image)

**Figure 3.8** Dielectric measurement system.

### 3.2.8 Vibrating sample magnetometer (VSM)

The vibrating sample magnetometer has become a widely used instrument for determining magnetic properties of a large variety of materials: diamagnetics, paramagnetics, ferromagnetics, ferromagnetics, and antiferromagnetics. It has a flexible design and combines high sensitivity with ease of sample mounting and exchange. Samples may be interchange rapidly even at any operating temperature. Measurements of magnetic moments as small as 5x10\(^{-5}\) emu are possible in magnetic fields from zero to 9T. Maximum applied fields of 2-3T or 9T are reached using conventional laboratory electromagnets and superconducting solenoids, respectively. Vibrating sample
magnetometers normally operate over a temperature range of 2.0 to 1050 K. Powders, bulk and thin films can be measured and studied. The block diagram Vibrating Sample Magnetometer is shown in Figure 3.9 and actual photograph of VSM is shown in Figure 3.10.

If a sample of any material is placed in a uniform magnetic field, created between the poles of an electromagnet, a dipole moment will be induced. If the sample vibrates with sinusoidal motion a sinusoidal electrical signal can be induced in suitable placed pick-up coils. The signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment, amplitude, and relative position with respect to the pick-up coils system.

The basic instrument includes the electromechanical system and the electronic system (including a personal computer), while the costumer should select the electromagnet or superconducting coil system with the appropriate bipolar power supply. Laboratory electromagnets or superconducting coils of various maximum field strengths may be used.

**Specifications:**

- Model- Lakeshore-7401
- Field range-0-1.2 T
- Temperature range-10K -350K
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**Figure 3.9** Block diagram of Vibrating Sample Magnetometer

**Figure 3.10** Vibrating sample magnetometer
3.2.9 Superconducting Quantum Interference Device (SQUID)

A Quantum Design Magnetic Properties Measurement System (MPMS), with a superconducting quantum interference device (SQUID) detector, provides the ultimate in resolution for magnetic measurements [19]. The SQUID unit can work in the temperature range between 1.9 and 400 K and under a maximum applied field of 7T. The heart of the MPMS is the superconducting detection coil. The detection coil is located at the midpoint of the superconducting solenoid, which is used to create the applied field. The SQUID sensitivity is usually of the order of $10^{-8}$ emu with an accuracy of 1%, which is more sensitive than other magnetometers like Vibrating Sample Magnetometer (VSM), $5 \times 10^{-5}$ emu. This high sensitivity makes the SQUID a perfect choice to measure small magnetic signals.

SQUID measures the magnetic moment by moving the sample through the detection coil. The magnetic moment of the sample creates a flux in the detection coil, which changes with the sample position. The flux is converted to a voltage by the magnetometer and the voltage versus sample position data is further used to extract the magnetic moment. The software package supplied with the MPMS analyzes the voltage versus sample position data and determines a value for the magnetic moment as a result of a fitting procedure between a theoretically expected curve and the experimental data. The schematic diagram of SQUID is shown in Figure 3.11 and actual photograph of MPMS SQUID system shown in Figure 3.12.
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**Figure 3.11** Schematic of SQUID Magnetometer

**Figure 3.12** MPMS SQUID Magnetometer.
3.3. Synthesis of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) where \( x = 0.1, 0.2, 0.3 \) and 0.35

The combustion synthesis or fire synthesis is also known as self-propagating high temperature synthesis (SHS). For combustion, an oxidizer, a fuel and the right temperature are needed. All these three elements make up a fire triangle. Fire can be described as an uncontrolled combustion which produces heat, light and ash shown in Figure 3.13. The process makes use of highly exothermic redox chemical reactions between an oxidizer and a fuel.

All self-propagating high-temperature synthesis reactions are redox reactions; however, all redox reactions need not be SHS reactions. For the reaction to be self-propagating the heat evolved should be more than the heat required for initiating the combustion. A redox reaction involves simultaneous oxidation and reduction processes. The definition of oxidation is addition of oxygen or any other electronegative element (nonmetal), while reduction is addition of hydrogen or any other electropositive element (metal).

\[ \text{temperature} \]
\[ \text{heat} \]
\[ \text{light} \]
\[ \text{fuel} \]
\[ \text{ash} \]
\[ \text{oxidizers} \]

**Figure 3.13** Combustion synthesis.

The term combustion covers flaming (gas-phase), smoldering (solid-gas) as well as explosive reactions. It can be linear combustion or volume combustion. In linear combustion the burning surface recedes from top to bottom in layers, whereas in volume combustion, the entire reaction mixture ignites to burn with a flame.
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The SHS process pioneered by Merzhanov has been used to prepare a large number of technologically useful oxide materials (magnetic materials, semiconductors, dielectric, sensors, etc.) and nonoxide materials (carbides, nitrides, borides etc.) by the solid-state reaction between the corresponding metals and nonmetals [20]. The process requires high-purity fine precursors, which ignite at temperatures >1000°C. The process is highly exothermic and self-propagating resulting in coarse products. This process has been successfully used in Russia to prepare hundreds of technologically useful materials [21], including the preparation of oxide materials in recent times. However, being a solid-state reaction it often does not produce homogeneous products and results in coarse powders. Here, the solution combustion approach is presented to prepare oxide materials of desired composition, structure and properties.

3.3.1 Solution combustion synthesis (SCS)

The solution combustion synthesis of oxide materials was unexpectedly discovered during the reaction between aluminum nitrate and urea. A mixture of Al(NO$_3$)$_3$.9H$_2$O and urea solution, when rapidly heated around 500°C in a muffle furnace foamed and ignited to burn with an incandescent flame yielding voluminous white product which was identified as $\alpha$-Al$_2$O$_3$ [22]. To understand the highly exothermic nature of this reaction, concepts used in propellant chemistry were employed [23]. A solid propellant contains an oxidizer like ammonium perchlorate and a fuel like carboxyl terminated polybutadiene together with aluminum powder and some additives. The specific impulse ($I_{sp}$) of a propellant, which is a measure of energy released during combustion is given by the ratio of thrust produced per pound of the propellant.

It is expressed as

$$I_{sp} = k \frac{T_c}{\sqrt{\text{Molecular weight of gaseous product}}}$$

.....(3.4)
The highest heat $T_c$ is produced when the equivalence ratio ($\Phi_e = \text{oxidizer/fuel ratio}$) is unity. The equivalence ratio of an oxidizer and fuel mixture is expressed in terms of the elemental stoichiometric coefficient.

$$\Phi_e = \frac{\sum \text{(Coefficient of oxidizing element in specific formula)} \times \text{(Valency)}}{(-1) \sum \text{(Coefficient of reducing element in specific formula)} \times \text{(Valency)}}$$

A mixture is said to be stoichiometric when $\Phi_e = 1$, fuel lean when $\Phi_e > 1$, and fuel rich when $\Phi_e < 1$. Stoichiometric mixtures produce maximum energy. The oxidizer/fuel molar ratio (O/F) required for a stoichiometric mixture ($\Phi_e = 1$) is determined by summing the total oxidizing and reducing valences in the oxidizer compounds and dividing it by the sum of the total oxidizing and reducing valences in the fuel compounds. In this type of calculation oxygen is the only oxidizing element; carbon, hydrogen, and metal cations are reducing elements and nitrogen is neutral. Oxidizing elements have positive valences and reducing elements have negative valences [24].

In solution combustion calculations, the valences of the oxidizing elements was modified and considered as negative, and the reducing elements as positive, similar to the oxidation number concept familiar to chemists. Accordingly, the elemental valency of C, Al, and H is +4, +3, and +1, respectively, and oxidizing valency of oxygen is taken as $-2$. The valency of nitrogen is considered to be zero [25].

### 3.3.2 Role of poly-vinyl alcohol

The poly-vinyl alcohol plays a dual role in the combustion process. Poly-vinyl alcohol has the ability of forming complexes with the metal cations in the solution ($\text{La}^{3+}$, $\text{Sr}^{2+}$, etc.). The complexation improves the solubility of the metal cations and prevents selective precipitation during the removal of water by boiling. The metal ions are kept in solution and randomly distributed until the point of ignition and oxide formation. This gives an oxide with great compositional uniformity. In addition to the complexation, poly-vinyl alcohol serves as a fuel for the combustion reaction. The combustion is driven by the...
oxidation of PVA by the nitrate ions. Hence, in this study we have used PVA as a fuel.

3.3.3 Salient features of Solution combustion synthesis

The exothermicity of the redox chemical reaction in SCS is used to produce useful materials. It has emerged as a viable technique for the preparation of advanced ceramics, catalysts, phosphors, pigments, composites, intermetallics, and nanomaterials. The salient advantages of SCS process are

- It is an easy and fast process that uses relatively simple equipment.
- Composition, structure and homogeneity of the products can be controlled.
- Formation of high-purity products are ensured by this method.
- High exothermicity of the metal nitrate–fuel reaction permits incorporation of desired quantity of impurity ions or dopants in the oxide hosts to prepare industrially useful materials.
- Formation of products of virtually any size (micron to nano) and shape (spherical to hexagonal) can be achieved by this process.
- This method involves lower costs of preparation compared to conventional ceramic methods.
- It is economically attractive and easy to scale up.
- Uniform distribution of the dopants takes place throughout the host material due to the atomic mixing of the reactants in the initial solution.

3.3.4 Experimental

Lanthanum manganites can be prepared by many different physical and chemical synthesis techniques and in various forms, including single crystals, polycrystalline ceramics and thick or thin films. Single crystals can be grown in several ways, for instance by the floating-zone method [26]. The polycrystalline samples can be prepared by solid state mixing, involving repeated steps of mixing, grinding and heating of oxides until a single phase
manganite is obtained. Polycrystalline manganites can also be synthesized by various wet-chemical methods [27,28]. Thick manganite films can be produced by spraying techniques and well-defined 2D-patterns can be obtained using screen printing techniques [29]. The thin films are usually grown by laser ablation (pulsed laser deposition) or sputtering using sintered polycrystalline targets [30]. Depending on the substrate, thin films can be prepared in epitaxial as well as polycrystalline forms [31]. However, the chemical synthesis [32], sol-gel [33], combustion thermal spray technique [34], flash-pyro phosphoric acid [35] citric gel method [36,37], hydrothermal synthesis [38,39], solution combustion method [40] have been applied for synthesis of nanocrystalline lanthanum based perovskites materials.

The Sr-doped lanthanum manganite samples under investigation in the present work were prepared by the solution combustion technique. The polycrystalline phase pure $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ samples were synthesized by solution combustion route. $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr(NO}_3)_2$ and $\text{Mn(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ of Alpha Aesar grade were used as precursor materials. These materials were dissolved in the double distilled water to form the solution of 0.1M. The equimolar solution of PVA was prepared in the distilled water. For the efficient burning process the used amount of fuel is very important. We first calculate the total oxidation/reduction valences of the fuel. The mixture of solution and fuel was prepared such that it contains the same oxidation and reduction valences [41]. It is mentioned here that the reduction valences of nitrogen and carbon have been taken as 0 and 4 respectively, by considering $\text{N}_2$ and $\text{CO}_2$ as the gaseous combustion product. The presence of these gaseous states in the evolved combustion product has been reported [42]. A schematic representation of the combustion process used in the current study is graphically shown in Figure 3.14.
Reaction for combustion

The possible reaction for the synthesis of La$_{0.65}$Sr$_{0.35}$MnO$_3$ is given below. According to propellant chemistry for getting the same oxidation and reduction valences in the solution, 2.325 mole % solution of PVA is required:

$$0.65 \text{La(NO}_3\text{)}_3 + 0.35 \text{Sr(NO}_3\text{)}_2 + \text{Mn(NO}_3\text{)}_2 + 2.325(-\text{C}_2\text{H}_4\text{O}) + 1.5 \text{O}_2 \rightarrow \text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3 + 4.65 \text{H}_2\text{O} + 2.325 \text{N}_2 + 4.65 \text{CO}_2 \quad ......(3.6)$$

Figure 3.14 The schematic representation of the combustion process.
The mixture of oxidants and PVA was kept onto a magnetic stirrer for 30 min to get a uniform mixing and then an ultrasonic treatment was given for 10 min. Finally, the mixture was kept onto a heating coil for the burning process. At the end, we get the output product as ash of $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ with $\text{N}_2$ and $\text{CO}_2$ along with vapors of $\text{H}_2\text{O}$.

Similarly, we have synthesized all the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples with $x=0.1-0.3$.

### 3.4 Characterization of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

#### 3.4.1 Thermogravimetric-differential temperature analysis of LSMO

The thermo-gravimetric and differential temperature analysis (TG-DTA) was carried out for phase confirmation of $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ from room temperature to 1000°C in air atmosphere. The TG-DTA curve for the precursor is shown in Figure 3.15 (a). The TG curve shows that, the initial weight loss is due to removal of water content. The second weight loss is attributed to detachment of nitrates group from the anion. After the 600°C, there is no weight loss in the material, which is attributed to material goes into desired stable phase. However the DTA graph shows the individual oxide formation with endothermic peak below 200°C. The exothermic peak at 400°C indicates the removal of nitrates groups from the precursor. The endothermic peak at 600°C confirms that there is stable phase formation occurs.

For the comparison, thermogravimetric analysis-differential temperature analysis on the as-prepared powder is carried out. Figure 3.15 (b) shows TG-DTA curve of $\text{L}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ as synthesized powder. There is atmospheric moisture content which gets removed at about 100°C. The actual reaction starts near about 275°C and ends at 575°C. The DTA shows sharp peak due to reaction of unburnt carbon content with oxygen to form $\text{CO}_2$ near 400°C. The second peak at 500°C shows that there is reaction with evolution of heat and material goes into desired stoichiometric form LSMO above 575°C.
Figure 3.15 TG-DTA of (a) Precursors (b) As synthesized LSMO powder.

From Figure 3.15 (a) and (b) we conclude that the stable phase formation for LSMO occurs above the 600°C. Also there may be some carbon traces in as combusted powder remains and observed in DTA of as combusted powder. Hence it is necessary to anneal the LSMO samples to get carbon free.
3.4.2 Structural analysis of LSMO

The crystallographic properties of La$_{1-x}$Sr$_x$MnO$_3$ for x=0.1-0.35 were investigated by means of x-ray diffraction. The detailed information on the structural changes associated with the variation of the Sr doping and annealing effect on lattice parameter was discussed.

The XRD patterns of samples M1, M2 and M3 annealed at 600 °C, 900 °C and 1200 °C respectively for 5 hrs are as shown in Figure 3.16 (a). These XRD patterns for the samples were compared with the standard JCPDS card (No: 47-0444) and all peaks or reflections such as (012), (110), (006), (024), (116), (214) and (220) were indexed. By XRD indexation the samples were shown to be well-crystallized perovskite oxides containing no impurity phases. Thus the phase La$_{0.9}$Sr$_{0.1}$MnO$_3$ was confirmed with rhombohedral crystal structure. The calculated lattice parameters were found to be $a=5.539$ Å, $b=5.531$ Å, $c=13.347$ Å which are in agreement with the standard value.

The average crystallite size was calculated by Scherrer formula. The Scherrer relation is used to calculate the crystallite size

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad \ldots\ldots (3.7)$$

where, $D$ is the crystallite size, $\lambda$ the wavelength of x-ray, $\beta$ the full width at half maximum of the (110) plane.

The crystallite size increases with annealing temperature. The observed crystallite size is in the range of 15-25 nm.

In similar fashion, we have plotted the graph of XRD for La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.65}$Sr$_{0.35}$MnO$_3$ as shown in Figure 3.16 (b), Figure 3.17 (c) and (d) respectively. We have got the rhombohedral crystal structure for all samples investigated in this work except one La$_{0.65}$Sr$_{0.35}$MnO$_3$ (M10) which is heat treated at 600°C. For this sample we got the Monoclinic crystal structure with lattice parameter $a= 5.2463$ Å, $b= 7.5243$ Å and $c=3.5245$ Å. The observed XRD pattern was compared with the standard JCPDS card (No-258-258).
Figure 3.16 Overlay of X-ray diffraction pattern of

(a) La$_{0.9}$Sr$_{0.1}$MnO$_3$, (b) La$_{0.8}$Sr$_{0.2}$MnO$_3$
Figure 3.17 Overlay of X-ray diffraction pattern

(c) La$_{0.7}$Sr$_{0.3}$MnO$_3$ and (d) La$_{0.65}$Sr$_{0.35}$MnO$_3$
The reflections from (020), (121), (220), (202), (222), (242), (402) and (442) planes are observed and indexed by comparing with standard data. Generally, to get the stable orthorhombic phase of Manganites synthesized by other method requires higher temperature ($1400^\circ C$-$1700^\circ C$). For monoclinic phase annealing temperature requires above the $800^\circ C$ [43], but in our case we get it at $600^\circ C$.

Thus, above analysis, we conclude that the gradual change of the XRD patterns, induced by increasing the amount of Strontium, was associated with a rhombohedral-to-monoclinic phase transition with decrease in unit cell volume. This conclusion is, of course, only valid for room temperature. The x-ray analysis did not provide any information on a possible temperature dependence on the structural properties of the samples.

### 3.4.3 Morphological analysis of LSMO

The surface morphology for the series of samples $La_{1-x}Sr_xMnO_3$ for $x=0.1$, 0.2, 0.3 and 0.35 were examined with a scanning electron microscope (SEM) (JEOL-JSM 6360) at an acceleration voltage of 20 kV and magnification of 20,000X.

The SEM micrographs of the samples of $La_{0.9}Sr_{0.1}MnO_3$ (M1, M2 and M3), $La_{0.8}Sr_{0.2}MnO_3$ (M4, M5 and M6), $La_{0.7}Sr_{0.3}MnO_3$ (M4, M5 and M6) and $La_{0.65}Sr_{0.35}MnO_3$ (M10, M11 and M12) synthesized by combustion method is shown in the Figure 3.18 and Figure 3.19. The study reveals that, all the samples show fine grains. It is observed that microstructures are strongly affected with the annealing temperature. It is seen that as annealing temperature increases the grain size rises. However, Sr doping at La site does not affect the morphology of all LSMO samples investigated in this study. The graining up of all samples takes place with good connectivity in grains without porosity.

The scanning electron micrograph for all samples shows that cluster of submicron size. This result confirms the particle size of LSMO synthesized by solution combustion route of the order of nanometric scale.
Figure 3.17 The scanning electron micrographs of (a) La$_{0.9}$Sr$_{0.1}$MnO$_3$ (M1, M2 and M3), (b) La$_{0.8}$Sr$_{0.2}$MnO$_3$ (M4, M5 and M6).
Figure 3.17 The scanning electron micrographs of (c) $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (M4, M5 and M6) and (d) $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ (M10, M11 and M12).
3.4.4 Elemental analysis of La$_{0.65}$Sr$_{0.35}$MnO$_3$ by EDAX

![Energy spectrum](image)

**Figure 3.20** EDAX spectra La$_{0.65}$Sr$_{0.35}$MnO$_3$ heat treated at 600°C

The elemental analysis was carried out for sample La$_{0.65}$Sr$_{0.35}$MnO$_3$ heat treated at 600°C. The graph x-ray intensity count with respect to the energy is shown in Figure 3.20. Inset of figure shows the surface area of the sample which is scanned for elemental investigation. The elemental composition obtained from EDAX analysis is shown in Table 1. The analysis performed on the surface of the heat treated pellet, shows that the average (La+Sr)/Mn atomic ratio is 1.07 which is very close to the expected one. Hence, the sample investigated for elemental analysis shows almost same the calculated stoichiometry with our original in sample.
Table 3.2 Concentration of La, Sr, Mn, and O atoms evaluated using EDAX.

<table>
<thead>
<tr>
<th>Element and Shell</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>26.14</td>
<td>66.09</td>
</tr>
<tr>
<td>Sr L</td>
<td>14.76</td>
<td>6.38</td>
</tr>
<tr>
<td>La L</td>
<td>36.90</td>
<td>11.22</td>
</tr>
<tr>
<td>Mn K</td>
<td>22.21</td>
<td>16.35</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

3.4.5 Transmission Electron Microscopy (TEM) of LSMO

The microstructure study and the crystallite size determination of particles were done by transmission electron microscopy (TEM). The transmission electron micrograph for La$_{0.65}$Sr$_{0.3}$MnO$_3$ sample heat treated at 600°C is shown in Figure 3.21 (a). From the TEM analysis, we confirmed the nano crystalline nature of LSMO with particles in a range 40-50 nm. The particle size of the powder was quite uniform and nearly no particle was over 50 nm.

The Selected Area Electron Diffraction (SAED) pattern for LSMO sample is shown in Figure 3.21 (b). The SAED image shows intense but spotty ring pattern which suggest the phase pure polycrystalline nature of LSMO synthesized by solution combustion route which is analogous to XRD study where we get crystallite size in the range of 15-25nm.
Figure 3.21 (a) TEM image of $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ sample heat treated at 600° (b) SAED pattern.

3.4.6 Fourier Transform Infra Red (FTIR) studies of LSMO

The FTIR studies have been carried out to study the bonding between metal ion and oxygen. The LSMO powders along with KBr powder mixed and pelletized. Here the KBr is added for the reference material. The overlay of $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ heat treated at 600°C, 900°C and 1200°C for 5 hrs is shown in Figure 3.22 (a) and overlay of LSMO for $x=0.1-0.35$ heat treated at 600°C shown in Figure 3.22 (b). The main absorption band around 600 cm$^{-1}$ corresponds to stretching of the metal–oxygen bond in the perovskite, which involves the internal motion of a change in Mn–O–Mn bond length in MnO$_6$ octahedral [44]. The two peaks at 860 and 1450 cm$^{-1}$ belong to SrCO$_3$ [45, 46]. The peak around 3000 cm$^{-1}$ corresponds to C-H stretching in the material. The peak at 1640 cm$^{-1}$ is due to the deformation mode of the absorbed molecular water and that around 3440 cm$^{-1}$ is due to O-H stretching of the same.
Figure 3.22 FTIR spectra of the LSMO nanoparticles (a) thermally decomposed for 5h at a 600°C, 900°C and 1200°C (b) LSMO with x=0.1, 0.2, 0.3 and 0.35 heat treated at 600°C.
This represents a crystalline powder containing wholly the LSMO perovskite structure [47]. From Figure 3.20 (a) it is observed that as annealing temperature increases the traces of SrCO$_3$ diminishes. The peak at 860 vanishes and at 1450 height of peak decreases. The substitution of Sr does not affect much more on the stretching of ion bonding.

The appearance of the stretching modes at transmission spectra indicates that the perovskite structure of LSMO has been formed at temperature of 600°C, 900°C and 1200°C which analogous to results obtained in X-ray diffraction study.

### 3.5 Conclusions

The various experimental techniques used in the present work are described with principal, construction and working. The polycrystalline LSMO samples have been synthesized by solution combustion method using PVA as a fuel and ion capping agent. The TG-DTA shows the stable phase formation occurs above the 600°C. Hence, all LSMO samples investigated in this study are heat treated at 600°C, 900°C and 1200°C. The structural analysis shows the all samples shows rhombohedral crystal structure. The surface modifications with annealing have been studied by scanning electron microscopy. The compositional analysis was carried out by EDAX and it is observed that LSMO sample is stoichiometric. The transmission electron microscopy shows the nanocrystalline nature of LSMO. The absorption band in FT-IR around 600 cm$^{-1}$ corresponds to stretching of the metal–oxygen bond in the perovskite, which involves the internal motion of a change in Mn–O–Mn bond length in MnO$_6$ octahedral.
Chapter III Experimental techniques and Synthesis of La$_{1-x}$Sr$_x$MnO$_3$

References