Chapter 2

2.1   Introduction

This chapter describes the methodology to synthesize the undoped and doped $RMnO_3$ (R=La,Gd) perovskites and discusses the experimental techniques used to characterize the synthesized samples. Synthesis of undoped and doped $GdMnO_3$ and $LaMnO_3$ are discussed in Section 2.2. In Section 2.3, we have explained the different characterization techniques used in the present work.

2.2   Powder Synthesis methods

Sol-gel and co-precipitation techniques used to synthesized the undoped and doped $GdMnO_3$ and $LaMnO_3$, respectively are explained below.

2.2.1   Sol-gel Method

In this work, the samples were synthesized using the sol-gel method (figure 2.1). For preparation of $GdMnO_3$ sample, gadolinium nitrate $(Gd(NO_3)_3.6H_2O$, SigmaAldrich,>99.9%) and manganese chloride $(MnCl_2.6H_2O$, Himedia,>98%) were taken in stoichiometry proportion and were dissolved in distilled water along with citric acid $(C_6H_8O_7)$. The cation to citric acid ratio was kept at 1:1. The solution was mixed with the help of magnetic stirrer taking a magnetic bead at 80 $^{\circ}$C for 20 minutes. Ethylene glycol was added dropwise to the mixed nitrate solution till the formation of a viscous gel. Afterwards, the gel was dried at 100 $^{\circ}$C for 6 hours and the powders were formed after grinding thoroughly. Finally, the synthesized powders were calcined at 1100 $^{\circ}$C for 5 hours to obtain the pure $GdMnO_3$. Fe and Cr doped $GdMnO_3$, are also synthesized after adding

required concentration of Ferric Nitrate (FeCl$_3$.6H$_2$O) or Chromium Chloride (CrCl$_3$.6H$_2$O, Himedia, >98%). The synthesis procedure remains same as undoped GdMnO$_3$. Flow chart for the synthesis of pure GdMnO$_3$ shown in **figure 2.1**.
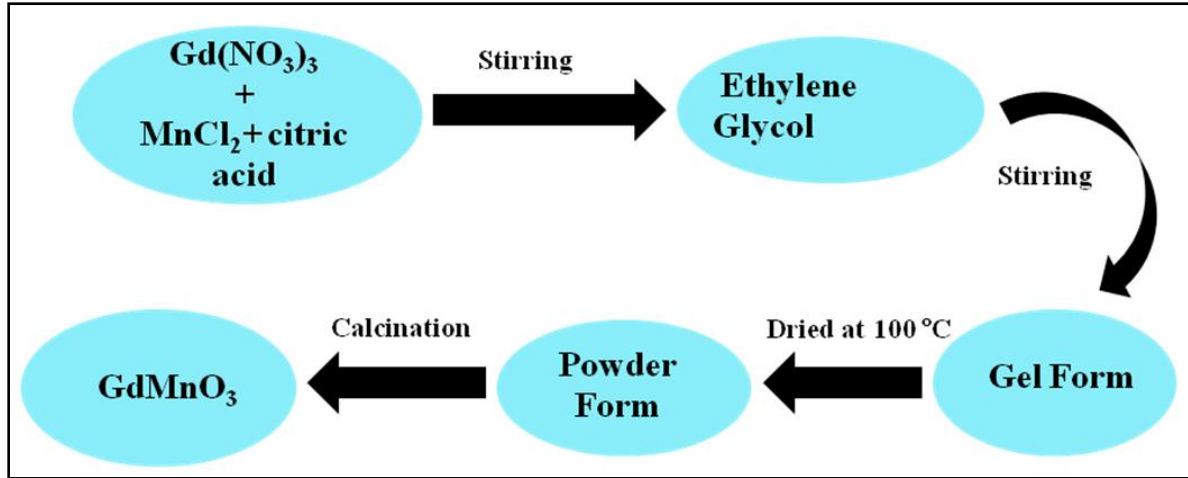

Figure 2.1 *Flow chart for the synthesis of pure GdMnO$_3$ using sol-gel technique.*

2.2.2 Co-precipitation Method

La$_{1-x}$MnO$_3$ (x=0 and 0.2) samples were synthesized by simple co-precipitation technique using stock solutions of 0.5 M of Lanthanum Nitrate (La(NO$_3$)$_3$.6H$_2$O) and 1 M of Manganese Chloride (MnCl$_2$.6H$_2$O). The preferred amount of Lanthanum Nitrate was taken and was subjected to stirring for 2 h using a magnetic stirrer. Then the required amount of Manganese Chloride was added slowly to Lanthanum Nitrate solution keeping that the mixed solution under continuous stirring for 1 h. Under stirring, to maintain the pH at 9.5 dilute aqueous ammonia (2 M) solution was added dropwise to the mixed solution. The precipitates were finally filtered, washed several times with distilled water followed by

acetone. The samples were dried in an oven at 60 ºC for 24 h and were calcined at 950 ºC for 5 h. Flow chart for the synthesis of LaMnO$_3$ is shown in **figure 2.2**.
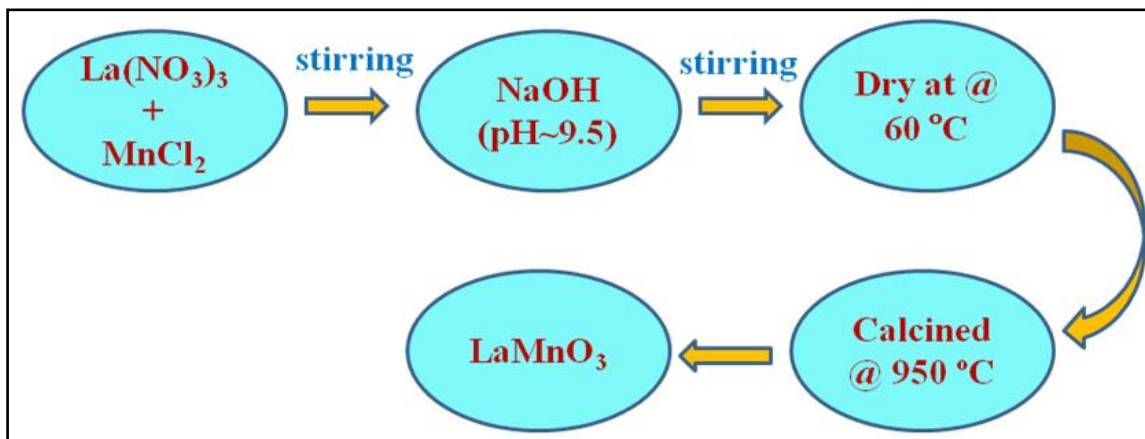

Figure 2.2 *Process flow of co-precipitation method for the synthesis of pure LaMnO$_3$.*

2.3 Characterization Techniques

Pure, Fe/Cr doped RMnO$_3$ (R=La,Gd) samples have been characterized employing appropriate techniques to analyze structure, magnetic and optical properties. The different characterization techniques utilized in the present thesis are briefly discussed below.

2.3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD), a non-destructive technique is the most widely used technique primarily employed to determine the structural properties of a particular material. In this technique, an electromagnetic wave having the wavelength of ~1 Å is diffracted from the crystal lattice planes oriented in different direction in crystal due to comparable order of magnitude of the X-rays wavelength and crystal lattice. XRD essentially facilitates the identification of different crystalline structure present in the materials. XRD is working on the principle of Bragg's law which states that the incident X-rays are diffracted from a set of equally spaced lattice planes in the crystal that interfere constructively. When the

35

path difference between them is an integral multiple of the X-ray wavelength, these diffracted X-rays interfere constructively. This can be mathematically expressed as follows:

$$2d_{hkl} \sin\theta = n\lambda \tag{2.1}$$

where, d_{hkl} is the interplanar distance (hkl are Miller indices), θ is the Bragg's angle, n is an integer indicating order of diffraction ($n = 1$ for XRD) and λ is X-ray wavelength. [78]. An illustration of the Bragg's law is demonstrated in **figure 2.3**.
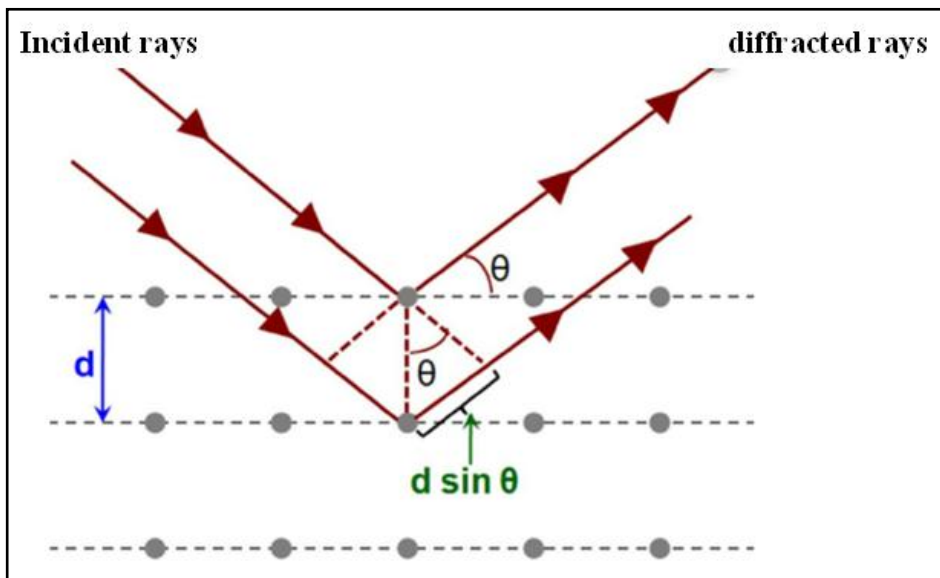

Figure 2.3 *Schematic representation of incident and diffracted X-rays from the crystal lattice.*

By following the constructive interference of Bragg's law, the diffraction pattern exhibits high intensity peaks at certain scattering angles. In general, the diffraction peaks are depend on the symmetry of structure e.g. the crystals which possess low symmetry structure e.g. monoclinic reveal several diffraction peaks because of numerous lattice

planes while in the case of cubic and tetragonal containing certain lattice planes, a few number of diffraction peaks are observed due to its high symmetry structure. The nature of diffraction peaks and their intensities are also correlated with the size and shape of particles in the crystal. XRD instrument having four different sections:

1) X-ray production

2) X-ray diffraction from the crystal

3) Detection of diffracted X-rays and

 4) XRD data recording and analysis.

In this instrument, the X-rays are produced when an accelerated electron beam of required energy is directed towards the copper metal target. The obtained collimated characteristic X-rays (K_α) of wavelength of 1.54 Å are utilized to characterize the material. Most of the diffractometer works on the para-focusing (or Bragg-Brentano) configuration. This geometry is the most common and well suited for different materials. By using the detector, the samples with flat surfaces are easily diffracted for collection of data. Diffracted beams are measured into a count rate which is essentially converted by the detector. The detector and sample can rotate by an angle 2θ and θ, respectively. Finally, the plot consisting of a series of diffraction peaks which are function of diffraction angle is realized that can be used for analysis of the crystal structure. Usually, the XRD patterns are recorded in the range of $2\theta = 5 - 120^o$.

In this work, XRD patterns were obtained by using a Rigaku Miniflex X-ray diffractometer with Cu $K\alpha$ (λ=1.54 Å) operating in Bragg-Brentano geometry. The indexing of XRD

patterns are done by using Joint Committee on Powder Diffraction Standards data (JCPDS). Using FULLPROF program for Rietveld refinement of XRD patternss, the different structural parameters like lattice constants, cell volume, bond lengths and bond angles are extracted for synthesized samples. This fitting technique is based on matching the suitable generated intensities with experimental data to determine the particular crystal structure of a specific space group.

2.3.2 Scanning Electron Microscopy (SEM)

For determining the topography and particle size, SEM is used. It primarily images the texture of the different surfaces. In this the incident electron beam falls upon the sample surface to ionizes the atoms as a consequence it can emit the loosely bound electrons called as the secondary electrons. These secondary electrons reveal relatively low energy within the range ~3 to 5 eV. For the information related to topography of the surface, such electrons are capable of marking the position of the beam very precisely. Due to their low energy the secondary electrons can be easily detected. A high contrast image is formed after scanning the beam onto a screen or computer monitor. With proper detection mode, remarkable contrast against topography is obtained. SEM shows good spatial resolution of the order of 10 nm or better thereby resolves most of the surface structures. We have utilized field emission-SEM, Nova of FEI make for recording images of specimens.

2.3.3 X-ray Photoelectron Spectroscopy (XPS)

XPS is also known as electron spectroscopy for chemical analysis (ESCA), which is used for the elemental analysis, oxidation state of the constituent elements and valence band structure by probing the surface of specimen. It is a surface sensitive technique so it provides essentially the relative composition of the constituents in surface regime. XPS is

working on the photoelectric effect in which the emission of electron are occurred when the core level electrons are excited by energetic X-ray photons of energy, hv. The kinetic energy (K.E.) of electrons emitted in such is expressed as follows:

$$\text{K.E.} = hv - \text{B.E.} - \phi \qquad (2.2)$$

where B.E. is the binding energy of an individual electron and ϕ is the work function. Explicitly, the photoelectrons are emitted from the core levels when the energy of X-ray photon is larger than the binding energy. The identification of these photoelectrons are based on their respective kinetic energy. The XPS spectra are drawn between the frequency of emitted electrons as a function of their K.E and intensity. The B.E. of different electronic states is calculated with respect to the Fermi energy level. For certain photon energy, the K.E. distribution of the photoelectrons implies the energy distribution of electronic states. These photoelectrons are usually scattered from nearby electrons, plasmons and/or phonons which slow down energetic electron after partially losing their energy. Due to significant loss in energy, the photo excited electrons do not pass through the specimen. This undesirable scattering of photoelectron results into unwanted secondary inelastic background intensity. Such scattering are more prominent within the low range of kinetic energy occurring because of strong electron-electron interaction. Although X-ray can penetrate up to large depth into specimen, only the photoelectrons originating from a depth of a few tens of angstrom can be detected due to high degree of scattering. After the collision or scattering, photoelectrons with sufficient kinetic energy surpass the work function barrier and reaches the detector. XPS consist three different parts such as:

(i) a photon source,

(ii) an energy analyzer for photoelectrons, and

(iii) an electron detector.

In general, the scattering and collisions between emitted electrons is reduced when the chamber is evacuated to ultra high vacuum. This enhances the mean free path of the emitting electrons which easily reaches to the detector. The monoenergetic soft X-rays more appropriate energy source for exciting the photoelectrons. A compatible electrostatic analyzer is used to analyze the excited photoelectrons. In this study, XPS measurements are performed on VSW and AMICUS make X-ray photoelectron spectrometer utilizing radiations of Al-Kα (1486.6 eV) and Mg-Kα (1253.6 eV), respectively. The sample preparation chamber is evacuated to ~10^{-8} Torr whereas the vacuum level of sample analysis chamber is maintained at ~10^{-9} Torr. The scanning is first carried out to collect the complete range of energy i.e. survey scan. Afterwards, for the precise elemental analysis and sample composition in our study, O 1s, Mn 2p and Fe 2p core level spectra are selectively recorded. All the recorded core level spectra are calibrated with respect to C 1s peak centered at ~284.8 eV.

2.3.4 Raman Spectroscopy

It is an non destructive technique which is based on inelastic scattering of monochromatic wavelength of a laser source. In inelastic scattering, the frequency of photons of the incident monochromatic light are changed after the interaction with the sample. Sample absorbed the photons of light and then re-emitted it. The frequency of the re-emitted photon is different from the incident light photon ie it is shifted up or down from incident light photon. This is known as Raman effect. This shift gives us the information

about rotational, vibrational and other low frequency transitions in molecules or solids. Raman spectroscopy of Horiba Jobin Vyon is used to characterize the various vibrational modes of the sample in the range 200-800 cm^{-1}.

2.3.5 Magnetic Measurements

Magnetic properties of the synthesized samples are investigated by means of field and temperature dependent magnetization measurements using Magnetic Properties Measurements System (MPMS3 of Quantum Design, USA). The magnetic moments are measured in this instrument with the help of vibrating sample magnetometer (VSM) and the superconducting quantum interference device (SQUID). This facility is avaiable at Centre Instrument Facility (CIF), IIT (BHU), India. The working principle of both VSM and SQUID is provided below.

i) Vibrating Sample Magnetometer (VSM)

VSM is capable of measuring the magnetic moment of the specimen maintaining excellent accuracy. The DC magnetization measurements of samples are performed with VSM operating between temperature range of 2 - 400 K and magnetic field of $\pm$ 7 Tesla. In this magnetometer, the measurement of magnetic moment with high precision is achieved with induction method. This method essentially involves the measurement of voltage which induces in a set of detection coils when the magnetic moment changes slightly in the sample. In practice, the measurement of induced voltage at the detection coil can be performed by vibrating speciemen with constant frequency under a uniform magnetic field. In a specimen, there exists numerous magnetic dipole. in the beginning, the specimen is fixed at the center of the detection coil. When it is displaced to a certain distance in time, t,

the change in flux (ϕ) inducing a voltage given by v = dϕ/dt which is measured in the detection coils. Usually, these detection coils are placed inside a solenoid producing the magnetic field. The resulting moment in specimen is then measured with respect to applied magnetic field [79].

Figure 2.4 *MPMS-3, Quantum Design (USA) used for magnetic measurement.*

ii) SQUID Magnetometer

For measuring the minute magnetic moment in the specimen, SQUID is the most suitable and sensitive technique. This device measures very small magnetic field with the help of superconducting loops which are prin Josephson junction. Specifically, SQUID indirectly

meausres the magnetic field of specimen. In general, when the specimen passes through superconducting detection coils connected with the SQUID via superconducting wires. This enables the flow of current from the detection coils to inductively coupled high quality sensors. The current from these coils is converted to equivalent voltage through SQUID. The whole assembly of instrumentation can be divied into following primary components: the main device i.e. SQUID, a magnetic flux transformer with appropriate detection coils, the superconducting magnetic coil, heat switches including suitable magnetic shielding configuration. Superconducting detection coils do not response to uniform and linear magnetic fields since the coils are set as second-order gradiometer having counter wound outer loops. When the local magnetic field changes, it produces a certain current in the detection coils. In practical situation, SQUID can response to every small change in the magnetic field. For this reason, the magnetic shielding is of utmost importance to prevent the sensor detecting stray fields arising from ambient or laboratory or the large magnetic fields originating from superconducting coil. The small area where magnetic field changes in detection coils, the heaters are used to remove the standing currents in the superconducting loops by raising them beyond their critical temperature. SQUID offers remarkable sensitivity of 5×10^{-8} emu and frequency range of 0.1 - 1 kHz. The measurement and removal of background ac phase shifts for each measurement is done through direct phase nulling technique. The rate of temperature change is 10 K/min from 300 to 10 K and then cool down very slowly from 10 to 2 K at 2 K/min. The aforementioned frequencies are used for ac susceptibility measurement.

2.3.6 Photoluminescence (PL) Spectroscopy

PL spectroscopy is the non destructive and widely used technique to study the electronic structure of different materials. When the light falls on the sample, sample absorbs the energy by the photo−excitation process and then emits this energy in the form of emission or luminescence. The photoluminescence is the emission of certain wavlength of light when the sample is exposed to light. The emissions of light are realized in different ways i.e. spectrally, spatially and temporally. The optical excitation of electrons is termed as the transfer of energetic electron to definte allowed excited states. The relaxation of these electrons towards ground or lower energy states can either emit light through a radiative process or may not produce light which is known as the non radiative process. The emitted light exhibits energy equal to the difference between final (excited) and initial (ground state) energy levels of the participating electrons. For the PL spectroscopy measurements, laser light or xenon lamp is used as the excitation source with variable energy. PL technique is also very much useful for analyzing the purity, crystalline quality and concentration of impurity and/or defects present in the material. An excitation spectrum is obtained for a particular emission wavelength which is partly similar to an absorption spectrum. At a certain wavelength known as excitation wavelength, the specimen can produce the emission spectrum characteristic of the materials.

PL spectrofluorometer (**figure 2.5**) measures and collects the spectra of fluorescence and phosphorence from the sample. During the fluorescence mode, the excitation and emission spectra are recorded for a range of wavelength. A standard fluorescence spectrometers contains following main components

Illumination source:- The source of light in PL, is a continuous source of light which is obtained either by broadband xenon lamp or by monochromatic laser. The light originating from light source is collimated with the help of a set of elliptical mirrors along with lenses and then it is delivered to the entrance slit of the excitation monochromator via optical fibers. A window made of quartz seperated he light source and excitation monochromator. This window is also used to release out the excess heating that may damage the light source.

Monochromators:- There are two monochromaters exist in PL one is excitation monochromator and other one is emission monochromator. These monochromators offer high resolution for the complete wavelength range.
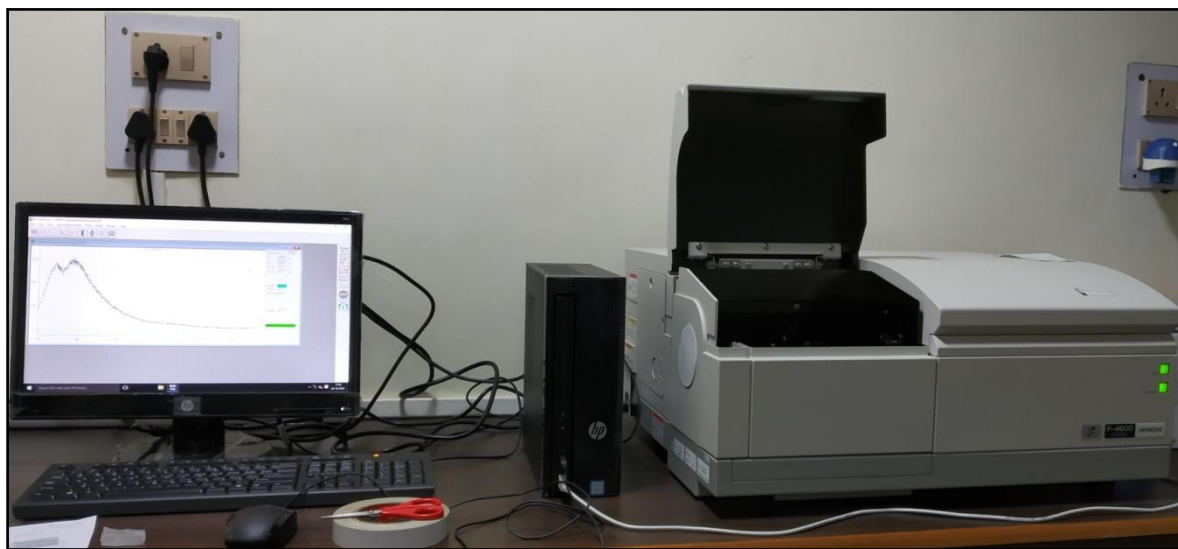

Figure 2.5 *Hitachi F-4600 used for Optical measurements.*

Gratings:- In the monochromator, for the dithe reflection grating is used to disperses the incident light occurring beacuse of the embedded vertical grooves and provides a good spectral resolution. MgF_2 layer onto these gratings prevents the unwanted oxidation.

Slits:- Entrance and exit slits are in both the monochromators for controlling the required amount of light. At the excitation monochromator, slit width allows certain band of light to transfer towards the sample. The slit at emission monochromator can be adjusted for signal intensity at the detector. The maximum intensity maintaining a high resolution over the whole spectral range is produced when an appropriate slit width is used.

Detectors:- There are two types of detectors are used in the spectrofluorometer one is reference detector and other is signal detector. A reference detector is used for the light source and signal detector is used transferring the signal to the photon counting module.

In present thesis work, the room temperature excitation and emission spectra have been collected from 150 W xanon lamp of Hitachi F-4600 spectrophotometer.