In this chapter the synthesis procedure and characterization of the selected polycrystalline compounds and related composite for the present work are briefly discussed. Different methods starting from XRD, SEM, PPMS SQUID/VSM, impedance and dielectric spectroscopy are described. Brief theory related to the experimental techniques and necessary schematic diagrams are also provided.

3.1. Sample preparation

Oxide materials are one of the foremost parts in the material science due to practical as well as industrial applications in day to day life. Hence the synthesis of such compound is of great importance in advancement of material science. It is better to use high purity starting materials to avoid the defects. It is very important to synthesize a single phase desired compound for proper investigation of the physical properties. The different parameters such as temperature, pressure, gas flow and time related to the reaction should be varied according to the necessities at the time of synthesis. There are several techniques which are generally used to prepare the oxide/polycrystalline...
compound such as mechanical method including solid state reaction, ball milling etc and chemical method including sol-gel, wet dry etc. Each and every method has some advantages as well as some disadvantages to get a quality product considering the purity, homogeneity, reactivity, particle size etc of the required compounds In this regard, the standard solid state reaction technique found to be simple, convenient and also low cost process among the other methods by means of performance, reliability, reproducibility and economy etc. The solid-state reaction method has also proved to be the most suitable to synthesize the reproducible compounds of oxide systems

3.1.1. Solid state reaction method

The most widely used method for preparing polycrystalline oxides in material science research is the direct reaction in the solid state, of a mixture of solid starting materials [1] As the desired phase is thermodynamically favored, the solids do not usually react together at room temperature over normal time scales and it is necessary to heat the starting materials at high temperatures to make the reaction at substantial rate. For this reaction, the rate limiting step is generally the solid state diffusion of the cations across the interface between the reactants High temperatures are required for this synthesis procedure to overcome the kinetic barriers and to enable the ions to jump out of their normal lattice sites and consequently diffuse through the crystal At such high temperatures, the reactivity of the crucible material must be considered. Normally common crucible materials for high temperature reactions are alumina, zirconia, magnesium oxide and platinum. These materials may contain other impurities to help in their processing So, contamination of the desired product by the crucible may not necessarily be by Al, Zr, or Mg

There are few important steps involved in solid-state reaction method to synthesize compounds All these steps are briefly described below

1) All the starting reactants such as high purity powders are preheated for suitable temperature and time to remove moisture. This is important for carbonates, nitrates before weighting to maintain the stoichiometric ratio in desired compounds

2) To facilitate the reaction process, it is essential to mix and grind the weighted powders thoroughly and gently for long duration to get a homogeneous distribution of the compounds in the solid mixture
3) The proper grinding of mixed powders using pestle-mortar reduces the particle size as much as possible. This is necessary for obtaining close contact among the atoms. The mixing decreases the length of the ions and increases the surface area for reaction.

4) This mixture of powders is then preheated in air/inert gas atmosphere according to the need at lower temperature for the first time. This initial heating of nitrates/carbonates containing mixtures, nitrogen/carbon dioxide is produced and escapes from the mixture.

5) A series of heating protocol in different atmosphere may be required to get the purity of phase.

6) It is always better to grind the powder each and every step during the series of heating.

7) The obtained fine powder is pressed into pellets before the final sintering of compound.

8) The pellets are sintered in a programmable furnace at required temperatures to obtain the desired structural phase. The samples are allowed to furnace cool. The reaction times are usually several hours to few days and it is best to repeat the process to insuire homogeneous samples.

9) The samples may have oxygen content slightly less than the required stoichiometry in oxide systems. To reach the optimum oxygen content, the samples have to be annealed, preferably in flowing oxygen. For appropriate oxygen content, the sintered pellets are usually kept for oxygen annealing at a desired temperature for a long period of time and then cooled down slowly to ambient temperature.

3.1.2. Sol–gel method

The sol-gel method is used to synthesize the materials either in bulk, films, fibers or powder forms [2, 3]. Regarding the microstructures, the sol-gel method yields mainly porous materials, dense materials like glasses and ceramics, organic-inorganic hybrids and nano-composites. Sol-Gel method has become an alternate technique to the conventional solid state reaction route, allowing more accurate control over the phase formation, desired stoichiometry and uniformity in particle size.
The main steps followed during this method are given below:

1) All the required raw materials including alcohol, concentrated/dilute acid and water are taken to prepare solutions. One or more solutions are prepared according to the need at ambient temperature. Generally, these solutions are made at room temperature.

2) Finally, the precursors are mixed in proper ratio in magnetic/mechanical stirrer for homogeneous solution and kept for some period of time.

3) The mixed solution is heated at desired temperature to change the solution to a high viscous gel.

4) The obtained gel is dried at certain temperature for some period of time.

5) This dried powder is grinded thoroughly by pestle-mortar and finally heat treatment is given to get the compound in a desired phase.

3.2. Characterization

3.2.1. Structural and morphological studies

Since the structural properties are closely related to the chemical characteristics of the atoms in the material, it is very essential to study structural properties of any kind of material to make sure about the structural phase of the compound before carrying out any experiments on that material. On the other hand, the morphological studies are also important to understand the internal structure, and how grain/grain-boundary is formed in thin films or in polycrystalline materials. There are a variety of techniques to investigate the structure and morphology of a material. These are used to as certain single phase samples and detect deviations from the main structure as well as extracting the actual structure. The different techniques have different advantages along with some disadvantages also. To study the crystalline nature of a material, two techniques are extensively used. 1) X-Ray diffraction (XRD) measurements and 2) Neutron diffraction (ND) measurements. ND is employed to determine the atomic and/or magnetic structure of a material. The technique of ND is almost similar to XRD but they provide complementary information due to their special scattering phenomenon. To study
morphology of the samples, generally, Atomic Force Microscopy (AFM) or Scanning Electron Microscopy (SEM) is broadly used. Transmission Electron Microscopy (TEM) is a useful device to find cross sectional view of the thin films, especially when thin films are irradiated or exhibit defects in the inner-structure. Energy-dispersive X-ray spectroscopy (EDAX) is used to confirm the composition present in the studied compound. Thermo Gravimetric Analysis (TGA) and Iodometric titration are commonly used to determine the oxygen stoichiometry in the materials. The iodometric titration is also used to study the concentration of different ions e.g. the ratio of Mn$^{3+}$ and Mn$^{4+}$ in doped manganites. Differential scanning calorimetry (DSC) is a technique to study thermal transitions such as the melting of a crystalline polymer, glass transition etc of the compound.

3.2.2. X-ray diffraction

The importance of diffraction techniques is embedded in the fact that diffraction is optimally sensitive to the periodic nature of the atomic structure of solid [4]. Real space imaging techniques on the other hand are sensitive to features that represent disruption from periodicity like lattice defects, dislocations and steps. Moreover, most of the real space imaging techniques is surface sensitive. The preparation of well defined and

![Figure 3.1: Schematic representation of diffraction of x-rays by crystallographic plane (Bragg's Law)](image)
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contamination free surfaces has always remained a challenge and is often a destructive process. Diffraction techniques are sensitive to the bulk of the material and are very simple to implement and are non-destructive processes. XRD technique is used basically to identify the phase purity, types of phases and crystallographic including bond length, bond angle variations and magnetic structure refinement etc. X-ray diffraction results from the interaction between X-rays and electrons of atoms. Depending on the atomic arrangement, interferences between the scattered rays are constructive when the path difference ($\Delta$) between two diffracted rays differs by an integral number of wavelength ($\lambda$). This selective condition is described by the Bragg equation

$$\Delta = 2ds \sin \theta$$

(3.1)

where $\theta$ is the incident angle of the X-rays and $d$ is the separation between successive planes. For constructive interference the path difference should be an integral number ($n$) of the wavelength i.e.

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

(3.2)

This is the Bragg’s Law.

However experimentally, the angle $2\theta$, which is the angle between the incident and the diffracted ray (Fig. 3.1), is measured rather than $\theta$. The detailed description of XRD is given in references [5, 6]. We have used a commercial diffractometer Rigaku, MiniFlex 600. In this instrument, the radiation source and a detector are fixed and the sample holder moves on the circumference of a vertical circle. The source here is a sealed X-ray tube generator consisting of a tungsten filament that emits electrons and a polished metal surface made of copper (Cu). X-rays are generated when the electrons are bombarded upon the Cu block.

3.2.3. Structure factors and Rietveld refinement

One method for evaluating the crystal structure from XRD data is Rietveld refinement [7-9]. The principle of the Rietveld method is to minimize a function, which represents the difference between a calculated profile and the measured data through an iterative least-squares method. Creating a calculated profile requires the input of the space group and corresponding lattice symmetries as well as a starting point for the lattice.
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parameters and atomic positions within the lattice. The program uses the space group to generate a reflection list and then computes the lattice parameters and structure factor ($F_{hk}$) from the provided model to match peak positions and amplitudes. The few parameters are then optimized to improve the reliability factor of the fit. In this dissertation, the FullProf program is used to refine XRD data of bulk samples [10].

3.2.4. Scanning electron microscopy (SEM)

A scanning electron microscope scans a focused electron beam over a surface to create an image. It forms a three-dimensional image on a cathode ray tube. The beam of focused electrons over an object interacts with the sample and producing various signals through both the scattered electrons by the object and the secondary electrons. This signal can be used to obtain information about the surface topography and composition. The surface homogeneity as well as the stoichiometry of a sample can be probed using an Electron Probe Micro-Analyzer (EPMA). Scanning electron microscope is used for studying the surface topography, microstructure, and chemistry of metallic and nonmetallic specimens at some magnifications. This technique is also used to quantitative chemical analysis.

3.3. Electrical and Magnetic measurement

All the prepared compounds under present studies are characterized for their electrical and magneto transport properties using the experimental techniques described in details below.

3.3.1. Transport measurements

i. Electrical resistivity

The electrical resistivity measurement is quite easy and simple to get much useful information including the metal to insulator transition, superconductivity, hopping mechanism etc. about the investigated sample. The different state of the material is explored and the phase transition in any type of crystal gives an easily accessible and accurate value of the critical temperature in addition to the conformation about the quality of the sample. It is so important to maintain the low contact resistance to measure the small resistance of any sample. Hence a standard four-probe technique is commonly used to measure the resistance of the samples [11]. For the electrical contacts silver paste and
thin cupper wire due to very less resistance is used. In this set up, two separate leads (outer probes) of thin copper wires pass a fixed current ($I$) through the sample and two other separate leads (inner probes) measure the voltage ($V$) as shown in Fig. 3.2. The whole assembly is put onto a sample holder where the wires are connected with leads through soldering to the measuring instruments. It is essential to keep the voltage probes between the current probes in a linear way. The sample chamber is vacuumed using rotary vacuum system. The samples may be cooled down using suitable coolant liquid (LN2 and He) and heated in a controlled way by using a heater. The resistance of the compound is measured in different protocol: cooling or heating or subsequent heating and cooling. Since most of the manganite compounds related to the thesis have low resistance at room temperatures, so a specific current source is applied to the sample through a current source. The current is passed through the outer probes (+I & -I) and resultant potential difference developed between two points is measured using the inner probes (+V & -V) as shown in the Fig. 3.2. The resistance ($R$) is accurately calculated by Ohm’s Law:

$$R = \frac{V}{I}$$  (3.3)
This can then be converted to resistivity ($\rho$) as

$$\rho = \frac{RA}{l} \quad (3.4)$$

Where $A$ is the cross-sectional area (as determined by the electrodes) and $l$ is the conductor length between the voltages probes.

To study magneto resistance (MR) characteristics of a compound, the resistance is measured by using the standard four probe method as explained in detailed in the previous section. But here the resistivity is measured of the system in presence of an external magnetic field. For MR vs $H$ behavior, the resistivity was measured at constant temperature with different magnetic field upto $\pm H_{\text{max}}$.

**ii. Thermoelectric power (TEP)**

The Seebeck coefficient also known as thermoelectric power is an extremely sensitive property whose study as a function of temperature would give valuable information on the electronic structure of the system under study. The Seebeck coefficient is defined in a simple way as follows

$$S = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$

where $\Delta V$ is the differential voltage developed across the sample for a temperature difference $\Delta T$.

Thermoelectric power can be measured using the differential technique wherein we create a temperature gradient across the sample and measure the voltage developed between the hot and cold ends of the thermocouple formed with a reference material. With the cold end of the sample connected to the positive of the measuring instrument the sign of the voltage developed gives the sign of the thermopower difference between the sample and the reference material.

**3.3.2. Quantum Design MPMS and PPMS**

Most characterization experiments have been performed using commercial equipment’s from Quantum Design, Inc. The resistivity is measured in absence and presence of applied magnetic field in a Quantum Design Physical Property Measurement System (PPMS). The Quantum Design PPMS basically is flexible and crucial instrument.
which represents a unique concept in laboratory equipment: an open architecture, variable temperature and magnetic field system, designed to perform a variety of automated measurements. The PPMS system has also been used as a base to provide temperature and magnetic field control for custom-made experimental set-ups for $\Delta T$ measurements and magneto electric measurements. The accessible magnetic field is 15T (cryogen-free high magnetic field system from Cryogenic Ltd., U.K.). Magnetic measurements are commonly collected using the magnetic property measurement system (MPMS). The MPMS is a superconducting quantum interference device (SQUID) magnetometer and provides temperature control from 1.7 K to 400 K (with furnace 300 K to 400 K) and magnetic fields of 5T or 7T. Magnetic measurements have also been done using a vibrating sample magnetometer (VSM). During the course of this thesis work, we have used PPMS facility (at UGC-DAE consortium for scientific research, Kolkata) for measuring resistivity.

### 3.3.3. Magnetic characterization methods

One of the main parts of the work in this thesis is based on macroscopic magnetic measurements using magnetization or susceptibility techniques. Magnetic measurements probe the magnetic state of the measured species. In DC measurements, the magnetic moment ($m$) induced in the sample is recorded in emu [cgs] or Am$^2$ [SI]. For a specific sample of known mass (volume), the magnetization $M$ in emu/g (emu/cm$^3$) [cgs] or Am$^2$/kg (A/m) [SI] can be obtained ($1$ Am$^2$/kg = 1 emu/g). Both quantities $m$ and $M$ depend on temperature, magnetic field $H$, time $t$ and pressure $p$. The characterization of the magnetic properties of a magnetic material depends on a thorough control of these parameters during the measurements. The type of magnetism of the studied material is manifested by the responses obtained. The most common way of probing the type of magnetism is to measure a hysteresis loop at constant temperature. When measuring the magnetic response as a function of temperature and magnetic field, not only these parameters but also the employed cooling protocol is important.

There is a number of different measurement protocols described below:
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1. Zero-field-cooled (ZFC) magnetization measurement: The sample is cooled in zero magnetic field and the magnetization is recorded in a magnetic field during reheating.

2. Field-cooled (FC) magnetization measurement. The sample is cooled in an applied magnetic field and the magnetization is recorded while it is cooling or on reheating.

3. Thermoremanent magnetization (TRM) measurement. The sample is cooled in an applied magnetic field and the magnetization is recorded in zero magnetic field under heating.

4. Isothermal-remanent magnetization (IRM) measurement: The sample is cooled in zero magnetic fields and the magnetic response is measured on reheating in zero magnetic fields. During the initial cooling a stop is made and a magnetic field is applied for the duration of the stop.

5. M-H loop measurement. The magnetization is recorded with the variation of magnetic field at different constant temperature.

3.4. Dielectric properties Measurement

Dielectric measurement is an important and versatile technique to explore the insulating or semiconducting systems. It has several applications in both basic science and engineering applications. It has some foremost advantages such as: broad frequency range, the simplicity of a measured cell, and the flexibility in shape, size, and state of matter of the investigated compounds. Dielectric spectroscopy basically measures the frequency or time dependent response of current and voltage of a sample with the applied electric field. A dielectric material has an arrangement of electric charge carriers that can be displaced by an electric field. The charges become polarized inside the sample to compensate for the electric field such that the positive and negative charges move in opposite directions. This response is related to the motion of free charge carriers or (permanent) dipoles.

Experiments can be conducted in the time domain as well as in the frequency domain. The samples are prepared in the parallel plate capacitor geometry. The simplest cell is done by painting the both sides of a pelletized sample with silver paste. Two thin copper wires are attached with a defined orientation on opposite surfaces of the measured
samples for making good electrical connections. Capacitance (C) and conductance (G) measurements are carried out in the frequency range from 42 Hz to 5 MHz using Impedance analyzer Hioki Model 3532-50. The dielectric properties such as relative permittivity, loss factor, impedance, and resistivity are calculated using the raw data and the pertinent sample dimensions.

3.5. References