Chapter 2

Experimental Techniques for Materials  
Synthesis and Characterization

Chapter II describes, in brief, various experimental techniques used for synthesizing bulk and thin films of manganites. This chapter includes details about synthesis and characterization techniques such as XRD (θ - 2θ and φ-scan), SEM, AFM, TEM, ρ - T, dielectric, I–V and EPIR (Electric pulsed induced resistance) used during the course of present studies.
Chapter 2: Experimental Techniques for Materials' Synthesis and Characterizations

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2.1 Introduction

In materials science, synthesis and characterization of various oxide materials are very important. Now a days, various kinds of synthesis methods and characterization techniques are being used. Generally, there are two types of synthesis methods (1) physical methods and (2) chemical methods. Physical methods include such as Pulsed Laser Deposition (PLD), RF supttring, Molecular Beam Epitaxy (MBE), Atomic Layer Deposition (ALD) and solid state reaction (SSR) method etc. Chemical methods include Sol-Gel method, chemical solution deposition (CSD), chemical vapor deposition (CVD), co-pricipitation method etc. Different characterization teciques such as X-ray diffraction (XRD), φ-scan measurement, Atomic force microscopy (AFM), scanneing electron microscopy (SEM), transmission electron microscopy (TEM), dielectric mesurement, two/four probe I–V measurement and electric pulse induced resistance (EPIR) measuremnts.

In this chapter, I have disscussed synthesis and various experimental techniques to be used for the sample characterization. It is divided into Five segments.

① Synthesis of PLD target bulk $Y_{0.95}A_{0.05}MnO_3$ ($A = Ca^{2+}, Sr^{2+}$) using Solid State Reaction technique.

② $Y_{0.95}A_{0.05}MnO_3$ ($A = Ca^{2+}, Sr^{2+}$) manganite thin films were deposited on Nb:SrTiO$_3$ (SNTO) substract using PLD technique.

③ SHI Irradiation experiment have been performed at Inter-University Accelerator Center (IUAC), New Delhi.

④ Nanostructured LaMnO$_3$ manganite synthesized using sol-gel technique.

⑤ To unerstand the structural, microstructural, surface morphology and transport properties of these samples various characterization techniques have been used.
2.2 Synthesis Techniques

2.2.1 Solid State Reaction (SSR)

Polycrystalline bulk samples are generally synthesized using conventional solid state reaction (SSR) [1]. The starting materials for the preparation bulk manganite samples are pure oxides, carbonates and nitrates. In SSR method, mainly four major steps are involved.

1. All the starting materials such as high purity powders of carbonates, oxides, nitrides, etc. are mixed for appropriate proportion.

2. Calcinations (Pre-heating) at high temperatures (heating of powders)

3. The proper grinding of mixed powders using pestle-mortar decreases the particle size as much as possible then pelletization using Dye-set (10 mm or 20 mm)

4. The pellets are sintered in a furnace, in air, at prominent temperature to get the preferred structural phase.

SSR method used for the preparation of PLD bulk target sample as given by:

\[ 0.95 \text{Y}_2\text{O}_3 (99.99\%) + 0.05 \text{CaO (99.99\%)} + \text{MnO}_2 (99.5\%) = \text{YCMO} \]

\[ 0.95 \text{Y}_2\text{O}_3 (99.99\%) + 0.05 \text{SrCO}_3 (99.99\%) + \text{MnO}_2 (99.5\%) = \text{YSMO} \]

For Preparation of PLD target, taken high quality (Sigma Aldrich) powder were weight and mixed as per above stoichiometric in SSR method. These powers were preheated then calcinations at 950°C for 24 hrs. Final product/pellet was sintered at 1100 °C for 48hrs in Air. Well sintered pellet (20mm diameter) was used as target in pulsed laser deposition (PLD) technique. The final product of SSR is usually in the form of powder or a sintered, polycrystalline piece.
2.2.2 Sol-Gel Technique

The sol-gel method is easy, cost-effective and chemical method to synthesis wide range of materials especially mixed oxide bulk, films, fibers or powder forms [2 – 4]. In this method, one can easily control the stoichiometry, play with oxygen in oxide materials and synthesized nanoparticles. The composite (nano composite, matrix) synthesized by sol-gel method. Sol-gel processes provide variety of precursors to select as starting materials covers the wide range of functional oxide materials such as high – temperature superconductors (HTSC), ferrites, manganites, multiferroics, etc.

Sol-gel process can be characterized by following steps.

1) Formation of stable precursor solution (sol) with the help of magnetic stirrer.
2) After, applying heat (fixed temperature) through magnetic hot plate, as a result, Gel formation along with increase in the viscosity of the solution.
3) Then, condensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network.

4) Drying of the gel, water contents are removed from the gel network. This process is complicated due to fundamental change in the structure of the gel. If isolated by thermal evaporation, the resulting monolith is termed a xerogel.

![Sol–Gel Method Diagram]

Figure 2.2: Typical flow chart of Sol-Gel method used for synthesis of LaMnO$_3$

2.2.3 Pulsed Laser Deposition (PLD)

Pulsed Laser Deposition (PLD) method is widely used for fabricating thin film layers of various functional materials [5,6]. Here, quite easy to produce multi-layer film, two or more, by controlling the number of pulses with a fine control of film thickness. In this technique, pulsed laser beam is focused inside a vacuum chamber to strike a target of the material. Then, material gets vaporized from the target (in a plasma plume) which gets deposited as a thin film on a substrate. Generally, thin films were deposited either in ultra-high vacuum or in the presence of a background gas, such as oxygen which is commonly used during synthesis process.
Figure 2.3: Schematic diagram of PLD set-up (Left side) and zoom view inside the vacuum chamber (Right side)

**Process**

This technique generally divided in to flowing steps:

- Laser absorption on the target surface
- Laser ablation of the target sample and creation of a plasma
- Deposition of the ablation material on the substrate
- Nucleation and growth of the film on the substrate surfaces.

Each of above steps is crucial for the crystallinity, film uniformity, quality of film: physical and chemical properties such as stress, adhesion, stoichiometry, film density, grain size and orientation.

**Advantages**

1. The main advantage is good stoichiometric control as compared to others deposition methods.
2. Control over the growth rate.
3. During deposition, target can easily be changed which helps to fabricate multilayers (for the case of heterostructures in multi target PLD set up).

Disadvantages

1. Formation of large particulates during the deposition
2. It can be used only for small area deposition.

2.2.4 Chemical Solution Deposition (CSD)

The CSD is very simple, cost effective chemical method where chemical solution is first prepared using the materials which is called precursors solution. This technique is frequently used to synthesize oxide, inorganic, metal organics etc based layers. Multilayer, composite, good stoichiometry, thickness control, etc are possible parameters for CSD method. Many papers are reported on chemically grown manganite based thin films. This technique is also known as the Sol-gel method because the ‘sol’ (solution) step by step evolves towards the formation of a gel like diphasic system. As the name suggest, sol-gel involves two types of materials or components, ‘sol’ and ‘gel’. Sol-gel when used for formation of thin films on substrate is called chemical solution deposition. Flow chart (figure 2.4) and general steps involved in CSD method, for synthesizing thin films of oxides materials, are described below.

Various steps involved in CSD technique

- Precursor’s solution
- Coating techniques
- Gel formation
- Removal of organic species
- Crystallization
2.3 Structural Characterization

It is very necessary to understand the structural phases of any samples in order to verify single phase structure before carrying out further characterization on the samples. Structural properties are closely related to the chemical characteristics of the atoms in the material and, thus, form the basis on which detailed physical understanding is built.
2.3.1 X-ray Diffraction (XRD)

X-Ray Diffraction (XRD) is an important characterization technique to determine the quality of crystal structure [7, 8]. In XRD, the X-rays which are used in laboratory based diffraction experiments are produced by a different processes that lead to monochromatic X-rays. During XRD, X-rays are coming from source and interact with sample (bulk, thin film and powder) that results in diffraction phenomenon.

![Schematic diagram of X-ray diffractometer](image)

An X-Ray diffractometer consists of mainly three components: X-Ray tube, sample stage and X-Ray detector as shown in figure 2.5. When X-Ray beam incidents on the sample and interacts with different atoms in the sample. When Bragg’s law is satisfied, the reflected beams are in-phase and interfere constructively. At angles of incidence, beams are out-of-phase and destructive interference of cancellation occurs. For a given set of lattice plane with an inter-plane distance of \(d\), the condition for a diffraction (peak) to occur can be simply written as

\[
2d \sin \theta = n\lambda
\]

This is known as the Bragg’s law. In the equation, \(\lambda\) is the wavelength of the x-ray, \(\theta\) is the scattering angle, and \(n\) an integer representing the order of the diffraction peak.
Figure 2.6: Schematic diagram depicting the Bragg’s law of X-ray diffraction

XRD techniques used to obtain information of the structure and characterization of solid. In the case of thin films, it is necessary that the scattered intensity contribution from the substrate should be minimized and this can be achieved by reducing the angle of incidence [Glancing incidence, Fig. 2.7 (b)].

Figure 2.7: Glancing incidence x-rays diffraction geometry for thin films.

The structure and phase purity of bulk as well as thin film samples were examined by the powder x-ray Diffractometer using Cu-Kα X-ray radiation of wavelength 1.5418Å.

2.3.2 φ – Scan Measurements

φ – Scan measurement is only possible for thin films, hetrostructures, devices and multilayers. After succesfully getting the information about crystal structure, i.e. phases, symmetry, etc, further to understand the in-plane or out-plane orientation and
crystallographic quality of film–substrate. By using the ϕ – Scan Measurement, one can confirm the crystal symmetry and either epitaxial or non-epitaxial film’s growth.

Figure 2.8: Schematic diagram depicting - θ, ψ and ϕ angles during XRD measurements of films

2.4 Microscopic Characterization

Similarly, microscopic characterization is also important for studies on the growth and packing density of grains in thin films or polycrystalline bulk materials. There are various techniques known to explore the science related to structure and Surface morphology of a material.

2.4.1 Atomic Force Microscopy (AFM)

To understand the surface morphology of thin films, one can use Atomic Force Microscopy (AFM) technique. This technique was first discovered by G. Binning and C. Gerber in 1985 [9]. AFM has a flexible cantilever ~ 100μm long, 10μm wide and 1μm in height attached with a piezodrive. A tip is mounted on cantilever as shown in fig.2.9, which can be brought close to sample surface. The resonant frequency is used to control the tip – sample interactions.
**Experimental Techniques for Materials Synthesis and Characterizations**

**Working**

When tip, close to the surface of the sample, experiences a repulsive force which results in the bending of the cantiliver for small amount of time interval, generates small deflections due to interaction between tip and sample. This interaction recorded by a position sensitive photodiode. By rastering the probe on sample surface and measuring the cantilever deflections surface image is obtained.

![Image of AFM (Left side) and Atomic Interaction (Right side)](image)

Figure 2.9: Image of AFM (Left side) and Atomic Interaction (Right side)

An AFM can be operated in three different modes such as contact mode, Non-contact mode and Trapping mode.

![Schematic diagram of AFM set-up and AFM Imaging Modes](image)

Figure 2.10: (A) Schematic diagram of AFM set-up and (B) AFM Imaging Modes
Contact mode

In this mode, the tip is in contact with the sample surface along with force, due to repulsive interaction between electron charge cloud of the tip atom and surface’s atom. The tip is repelled back which bend the cantilever and deviate the direction of the laser beam. In this case, sample can be damaged slightly due to forcing of the tip into sample.

Non-contact mode

In this case, the tip moves at some small amount of distance away from the sample surface. Therefore, it can not damage the sample. Here, polarization phenomenon occurs due to dipole-dipole interaction of two atoms.

Trapping mode

This mode is combination of contact and non-contact modes. The resolution quality is better in contact mode as compared to non-contact mode, because in contact mode, the strong interaction between the tip and surface atoms is much more sensitive. With trapping mode, high resolution advantage of contact mode and non-destructiveness of non-contact mode are achieved.

2.4.2 Scanning Electron Microscopy (SEM)

SEM is optical microscopy for studying the texture, topography and surface features of powders (or pellet) of solid sample. A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning over it with a high energy focused beam of electrons.

Principle

Electrons accelerated from the electron gun through 5 – 500 KeV, are focused to a small spot having ~ 50 – 500 Å diameter on the sample surface. These electrons can penetrate the depth of the sample around ~ 1µm. The incident electrons penetrate deeper into the sample and lose their energy via lattice vibration of radiation damage and are unable to escape from the sample. The main advantage of SEM is for surveying materials under the high magnification and giving information on sizes, shapes and compositions as seen from solid surface [10].
Working

The emitted electrons interact with the target sample, where resultant back scattered electrons are detected under the vacuum $10^{-2} – 10^{-3}$ Pa. The signal from scan generator along with applied signal from the electron collector generates the image of sample surface. Here, one disadvantage is insulating sample can not be performed directly because they get charged when electron incident and image becomes blurred. Therefore, insulating solids are coated with a very thin metal film like gold.

2.4.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which very high energy electrons ~ (50 keV) are used and pass through a series of magnetic lenses. TEM can be operated through basic components such as electrons source, condenser lens, sample, objective lens, diffraction lens, intermediate lens, projectile lens and a fluorescent screen in the given order. Sometimes, addition of more lenses in order to improve the image quality and resolution. Generally, all the lenses are electromagnetic whose focal lengths are varied to obtain optimized images rather than moving the lenses themselves as is done in an optical microscope [10].
When high energetic electron interaction, pass through the sample, then, start scattering phenomenon via elastic scattering due to no energy loss and inelastic scattering due to interactions between primary electrons and sample electrons at heterogeneities such as grain boundaries, dislocations, second-phase, defects, etc. Resulting images will be generating on the computer screen.

**Application**

- Provide high resolution images along with internal structure of a sample.
- To obtain an internal image of a sample opens new possibilities for what nature of information can be gathered from it.

**2.5 Transport Characterizations**

To understand the charge transport properties of thin films, devices, composites and hertostrcutures for determining their applicability and usefulness with the help of D.C. two/four probe resistivity method, transport measurements can be performed [11]. The samples, in the present thesis, were characterized for their transport properties by the D.C. two-probe resistivity technique as described below.
2.5.1 D.C. Two Probe Resistivity Method

In this method, current is measured as a function of voltage and the resistance will be included in a contribution from the probes. Electrical resistivity is inversely proportional to the carrier density and carrier mobility. Various types of methods have been suggested to measure the transport properties which depending upon sample such as thin films, bulks and devices, as well as the value of resistance.

During my measurements, source meter 6517B was used. Applied voltage in the form of sweeping cycle (0V→+V→0V→-V) across junction, measured current in 0.1 V steps.

![Image of a source meter and current perpendicular in plane (CPP) geometry](image)

Figure 2.13: Source meter (Left Side) and Current Perpendicular in plane (CPP) geometry (Right Side) for I-V measurements.

During the present work, I-V hysteresis behavior of p-n junction diodes was studied using the d.c. two probe method by varying sweeping bias voltage cycles: 0V → +10V → 0V → -10V → 0V. Figure 2.12 show the current perpendicular in plane (CPP) geometry for I-V measurements.

2.6 Electrical Characterizations

2.6.1 Dielectric measurements

Dielectric constant, property of an electrical insulating material, equals to the ratio of the capacitance of a capacitor filled with the given material to the capacitance of an
identical capacitor in a vacuum without the dielectric material. When a dielectric material is placed in an electric field, electric charges do not flow through the material, but, only slightly shift from their average equilibrium positions due to dielectric polarization. In dielectric polarization, positive charges are shifted toward the field and negative charges shift in the opposite direction.

A common, yet notable, example of a dielectric is the electrically insulating material between the metallic plates of a capacitor (figure 2.14).

Dielectric constant for the sample can be calculated by measuring the capacitance of the material. The temperature and frequency dependent capacitance can be measured using Agilent E4980A precision LCR meter. The value of the dielectric constant ($\varepsilon'$) was calculated using the formula;

$$\varepsilon' = \frac{c}{c_0}$$

where $\varepsilon'$ is the real part of the dielectric constant, $C$ is the capacitance of the material inserted between the electrodes and $C_0$ is the capacitance of the air medium or no medium between the electrodes. The $C_0$ for the parallel plate capacitor can be calculated using the following equation

$$C_0 = \varepsilon_0 A / t$$

where $\varepsilon_0$ is permittivity in vacuum $\sim 8.854 \times 10^{-12}$ C$^2$/N.m$^2$, $t$ is the sample thickness and $A$ is the area of the specimen in square meter. Using these two equations, the dielectric constant can be calculated as
\[ \varepsilon' = C \times t / \varepsilon_0, A \]

The imaginary component of dielectric constant (\( \varepsilon' \)) can be calculated using the formula,

\[ \varepsilon'' = \varepsilon' \tan\delta \]

where, \( \tan\delta \) is loss tangent, preoperational to the “loss” of energy from the applied field into the sample (in fact, this energy is dissipated into heat) and therefore denoted as dielectric loss.

2.6.2 Electric Pulsed Induced Resistance (EPIR) Switching Measurements

A novel electric pulsed induced resistance (EPIR) switching observed in manganite based thin films, having general formula \( \text{REAMO} \) (\( \text{RE} \) is rare earth and \( \text{M} \) is transition element) [12]. Here, Resistance is changed under the application of electric field. In EPIR, two independent state of resistance can be observed, i.e. low resistance state (\( R_L \)) and high resistance state (\( R_H \)) under the application of electric pulse. Other models/mechanisms such as charge trapping/de-trapping, formation of schottky barrier and creation of crystalline defects by the applied electric field, etc have also been reported.

![Figure 2.15: Room temperature EPIR switching behavior.](image-url)
Figure 2.15 Shows a typically graph of resistance vs. pulse nummber for manganite based oxide material collected under 5V & 10V pulses under zero applied magnetic field. This graph shows the two stable resistance states which make this material a poystential candidate for pratical application. Many machnisms have been proposed to explain/ understand the EPIR switching behavoir in manganites. All the mechanisms can be classified in the two catagories: forming and rupture effects required for resistance change under the application of electric pulse along with polarity in binary oxide materials.

2.7 Irradiation experiement at IUAC, New Delhi

Swift heavy ion (SHI) irradiation is one of the most important tools to create artificial defects, to modify the interface between film and substrate and to change electrical and magnetic properties of mixed valent manganites. Recently, Eesh et al [13] have studied charge transport mechanism in chemically grown manganite based thin films. They have studied the charge transport mechanisms by using various theoretically models and understood the role of SHI irradiation 200 MeV Ag$^{+15}$ ion having fixed 5E10$^{11}$ ions/cm$^2$ fluence in the order of different thicknesses of La$_{0.7}$Pb$_{0.3}$MnO$_3$ manganite films. Ravalia et al [14] have reported SHI that irradiation creates the structural defects in PLD grown BiFeO$_3$ thin film and studied electrical, polarization and magnetization properties. Ravalia et al [15] have also studied transport properties of La$_{0.6}$Pr$_{0.2}$Sr$_{0.2}$MnO$_3$/SrNb$_{0.002}$Ti$_{0.998}$O$_3$ thin film devices by SHI irradiation. They have discussed SHI irradiation induced modifications of interface/depletion region between film and substrate. During Ph.D. work, I would like to understand the role of SHI irradiation in resistive switching phenomenon. Shibuya et al [16] investigated the effect of defects on resistive switching characteristics of Sr$_2$TiO$_4$ Thin films. Further, they have used the role of defects for the RS effect. In presently study, the effect of SHI irradiation on the modifications of resistive switching mechanism of manganite based thin film devices. Joshi et al [17] have reported the resistive switching phenomenon induced by SHI irradiation in Li$^{+3}$ ions doped in NiO thin films grown on MgO substrate by using chemical method. To change the defect density, SHI irradiation has been used, resulting the key role for existence of resistive switching phenomena. Bhavsar et al [18] have
studied the resistive switching effect in La$_{0.7}$Sr$_{0.3}$MnO$_3$ manganite based thin film devices. They observed RS ratio ($R_{\text{high}}/R_{\text{low}}$) of pristine and irradiated film which is $\sim$ 52% and $\sim$ 330%, respectively. Irradiated films reveal that high RS ratio compared to pristine, which suggest that SHI irradiation create more defects density in the film.

During my Ph.D. work, 200Mev (100MeV) Ag$^{15+}$ (O$^{7+}$) ions irradiation studies have been carried out on Y$_{0.95}$A$_{0.05}$MnO$_3$ (A=Ca$^{2+}$, Sr$^{2+}$) manganite films using Material Science Beam Line of pelletron facility available at Inter University Accelerator Center (IUAC), New Delhi.

Figure 2.16: Photograph of high vacuum chamber available at material science beam line at IUAC, New Delhi

Some of the important features involved in this set-up are as follows:

1. Required high vacuum in chamber ($10^{-6}$ mbar) to avoid any collision of the ions with the gas molecules. (see in figure 2.16)

2. Films were mounted on the ladder, made up of copper block and stepper motor is used to provide up and down motion to the ladder
During irradiation experiment, we can easily observe the sample on television in data room with the help of CCD camera.

All the Films were irradiated with (200 MeV) 100MeV O^{17} (Ag^{+15}) swift heavy ions (SHI) with different ion fluencies using 10mm × 10mm ion beam scan area on the surface of the films using 15UD Tandem Accelerator, IUAC, New Delhi facility.

In order to irradiate the oxide thin films, following steps have been followed prior to load the samples in the irradiation chamber:

- Calculate the total numbers of ions falling on the sample using current integrator and pulse counter using the equation

\[
N_{\text{of counts}} = \frac{Dose \times q \times 1.6 \times 10^{-19}}{Pulse \, Height \, t}
\]

\[
Time (\text{Sec}) = \frac{Dose \times Area}{Current \,(\mu A) \times 1.6 \times 10^{-15}}
\]

Using stepper motor, fix the sample position according to scanning area on CCTV camera and start the beam for irradiation of sample films.

- In the present work, all the films were irradiated with 200 MeV (100 MeV) Ag^{+15} (O^{+7}) swift heavy ions (SHI) with different ion fluencies using 15UD Tandem Accelerator, IUAC, New Delhi facility. With the help of Stopping Range of Ions in Matter (SRIM) [19] software was used to calculate the depth distributions of the irradiated ions.

- For 200 MeV Ag^{+15} ions irradiation on Y_{0.95}Sr_{0.05}MnO_{3} (YSMO), the electronic energy loss (Se) and the nuclear energy loss (Sn) are calculated as 14.28 keV/nm and 38.46 eV/nm, respectively. The projected ion range in YSMO is 22.26 μm.

- For 100 MeV O^{+7} ions irradiation on Y_{0.95}Ca_{0.05}MnO_{3} (YCMO), the electronic energy loss (Se) and the nuclear energy loss (Sn) are calculated as 0.8149 keV/nm and 0.4555 eV/nm, respectively. The projected ion range in YCMO is 85.64 μm.
References


