CHAPTER-2

MATERIALS AND EXPERIMENTAL METHODS
# CHAPTER 2

## Materials and Experimental methods

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2. MATERIALS AND EXPERIMENTAL METHODS

This chapter deals with the description of different materials and experimental methods involved to achieve the objectives of this investigation. The sample preparation and other characterisation techniques are discussed in detail.

2.1 PREPARATION OF PEROVSKITE MANGANITE MATERIALS

2.1.1 PREPARATION OF PEROVSKITE MANGANITE MATERIALS BY SOLID STATE METHOD

Solid state method involves physical mixing of hydroxide, oxide, carbonate, nitrate or sulphate raw materials followed by high temperature treatment, for a lengthy period. This method results in powders with coarse grained, agglomerated structure with very low surface. High temperature leads to poor sintering behavior, inhomogeneous microstructure, possibly abnormal of grain growth and lack of control of cation stoichiometry.

Doped lanthanum manganite with the composition, La$_{0.6}$Ba$_{0.4-x}$Ca$_x$MnO$_3$ ($x = 0.005, 0.01, 0.015$ and $0.020$: hereafter termed as SS-LBCM1, SS-LBCM2, SS-LBCM3 and SS-LBCM4 respectively) was prepared by a solid-state (SS) reaction method. The stoichiometric quantity of analytical grade lanthanum nitrate (99%, Merck), Barium Carbonate (99.9%, Qualigens), Calcium Carbonate (99.5%, SRL 99.5%) and Manganese carbonate (99.9%; Sigma-Aldrich) were mixed in an agate mortar. The mixed powder was grind to obtain fine powders. The grind mixture was calcinated at 873 K in air for 2 h
and then further grinds to obtain a homogeneous mixture. The grind mixture was again calcinated at 873 K in air for 2 h and then further grinds to obtain a homogeneous mixture. The powder was further sintered at 1273 K for 12 h in atmospheric air. Every time before sintering, the grinding is adopted to get the uniform mixture of the composition. During the sintering process, the dopants get disperse to maintain the phase purity of the sample. The flow chart of the synthesis process is as shown in Fig. 2.1. Similar procedures were adopted to prepare the lead and strontium doped lanthanum manganites. Table 2.1 shows the various compositions of divalent doped lanthanum manganite samples prepared by above-mentioned methods.

Fig. 2.1 Flow chart for the preparation of manganite by SS method.
2.1.2 PREPARATION OF PEROVSKITE MANGANITE MATERIALS BY SONOCHEMICAL METHOD

The conventional solid state method involves inhomogeneity of the product, growth of particles to larger scale with low surface area, presence of defects. The problem of inhomogeneity could be lessened by the use of sonochemical method. In sonochemical method the mixing of the reactants will be done with very high speed, which reduces the agglomeration of the particles and fine powder samples can be obtained [124, 125].

The nanocrystalline manganite samples of composition La$_{0.6}$Ba$_{0.4-x}$Ca$_x$MnO$_3$ ($x = 0.005, 0.01, 0.015$ and $0.020$; hereafter termed as SC-LBCM1, SC-LBCM2, SC-LBCM3 and SC-LBCM4 respectively) were prepared using a sonochemical (SC) method. The stoichiometric amounts of analytical grade chemicals such as lanthanum nitrate (99% Merck), Barium Carbonate (99.9% Qualigens), Calcium Carbonate (99.5% SRL 99.5%) and Manganese carbonate (99.9%; Sigma-Aldrich) were used as a precursor. Initially, manganese carbonate was sonicated in dilute nitric acid for 20 min to convert the insoluble carbonate into soluble nitrate. A highly intense sonication was carried out with a high intensity horn made up of titanium operated at a frequency of 20 kHz and temperature 353 K (Sonics, USA). To this mixture, lanthanum nitrate, barium carbonate and calcium carbonate salt solutions were added frequently during the sonication process. After the reaction, the pH value of the solution
was adjusted to ~7 by adding sodium hydroxide (NaOH) drop wise under constant sonication speed. After sonication, the solution was allowed to dry in a hot air oven maintained at 403 K for 24 h. The residue formed was collected and then calcined in air at 873 K for 2 h to obtain the required composition and then further grinds to obtain a homogeneous mixture. The powder was further sintered at 1273 K for 12 h in atmospheric air. Fig. 2.2 flow chart explains the SC method of preparation. Similar procedures were adopted to prepare the lead and strontium doped lanthanum manganites. Table 2.1 shows the various compositions of divalent doped lanthanum manganite samples prepared by above-mentioned methods.

In both the methods especially for LPCM samples, the stoichiometry of lead was maintained by keeping pH of the samples in the range of 3 – 7.4 [126]. NaOH / NH₄OH were used drop wise periodically to maintain this pH value in SS method and appropriate quantity of NaOH solution of 6 M was used in SC method. During the reaction, temperature increases makes the pH to decrease, hence by adding base, the decreased pH was again brought to almost same level.
Fig. 2.2 Flow chart for the preparation of nano perovskite manganite
Table 2.1 Composition of the prepared perovskite samples along with its sample code

<table>
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<th>Sample Code</th>
<th>Nominal Perovskite Compositions</th>
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<tr>
<td></td>
<td>La₂O₃</td>
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<tr>
<td>Solid State (SS) method</td>
<td>Sonochemical method (SC)</td>
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<tr>
<td>Series I: La₀.₆Ba₀.₄₋ₓCaₓMnO₃ (x = 0.005, 0.01, 0.015 and 0.020)</td>
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<tr>
<td>SS-LBCM1</td>
<td>SC-LBCM1</td>
</tr>
<tr>
<td>SS-LBCM2</td>
<td>SC-LBCM2</td>
</tr>
<tr>
<td>SS-LBCM3</td>
<td>SC-LBCM3</td>
</tr>
<tr>
<td>SS-LBCM4</td>
<td>SC-LBCM4</td>
</tr>
<tr>
<td>Series II: La₀.₆Pb₀.₄₋ₓCaₓMnO₃ (0.005, 0.01 and 0.015)</td>
<td></td>
</tr>
<tr>
<td>SS-LPCM1</td>
<td>SC-LPCM1</td>
</tr>
<tr>
<td>SS-LPCM2</td>
<td>SC-LPCM2</td>
</tr>
<tr>
<td>SS-LPCM3</td>
<td>SC-LPCM3</td>
</tr>
<tr>
<td>Series III: La₀.₆Sr₀.₄₋ₓCaₓMnO₃ (x = 0.005, 0.01, 0.015 and 0.020)</td>
<td></td>
</tr>
<tr>
<td>SS-LSCM1</td>
<td>SC-LSCM1</td>
</tr>
<tr>
<td>SS-LSCM2</td>
<td>SC-LSCM2</td>
</tr>
<tr>
<td>SS-LSCM3</td>
<td>SC-LSCM3</td>
</tr>
<tr>
<td>SS-LSCM4</td>
<td>SC-LSCM4</td>
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The obtained powder samples were characterized using X-ray diffraction (XRD). Fourier transform of infrared spectroscopy (FTIR), scanning electron microscope (SEM), transmission electron microscope (TEM). The magnetic and optical properties of the samples were carried out using vibrating sample magnetometer (VSM) and spectroflorolog instruments.

2.2 CHARACTERIZATION

2.2.1 POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction (XRD) is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as ‘phases’ of compound present in powder and solid samples. The basic law involved in the diffraction method of structural analysis is the Bragg’s law. The corresponding Bragg’s expression is given by \( n\lambda = 2dsin\theta \), where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of X-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle.

The structural characterization was done by recording the X-ray diffraction (XRD) pattern of the samples. A given substance always produces a characteristic diffraction pattern whether that substance is present in the pure state or as one of the constituents of a mixture of substances. This is the basis for the diffraction method of chemical analysis. Experimentally obtained diffraction patterns of the sample were compared with the standard powder diffraction files published by the 'International Centre for Diffraction Data' (ICDD/JCPDS). X-ray
diffraction studies provide information about the crystal structure, orientation, average crystalline size and stress in the powder.

Fig. 2.3 Schematic diagram of X-ray diffractometer

In general a powder sample is prepared and loaded into the X-ray diffractometer and it is rotated through a chosen 2θ angle, as shown in the Fig.2.3. The incident x-ray beam is reflected out of the sample and may go through several slits (collimator and filter) before entering into a detector which registers the intensity at an angle 2θ with respect to the sample plane. At certain characteristic angles for each material the Bragg diffraction condition meets and large intensities of the reflected beam will be detected. These intensities are seen as peaks in a plot of 2θ Vs Intensity. The peak positions, peak shapes and relative intensities are directly correlated.
to crystallographic spacing, phase and grain size of particles. Compared with ordinary chemical analysis the diffraction method has the advantage of fastness and requires only very small quantity of sample and is non-destructive [127]. The powder X-ray diffraction (XRD) studies were carried out using Phillips X-ray diffractometer (model PW 3710) with Cu Kα radiation (λ=1.5405Å).

2.2.2 ESTIMATION OF CRYSTALLITE SIZE AND MICRO STRAIN FROM XRD DATA

XRD data can be used to estimate grain size or crystallite size via Scherrer’s equation,

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] (2.1)

where \( \lambda \) represents the wavelength of the X-ray radiation, \( \beta \) is the full width at half maximum (FWHM) of diffraction peak (in rad) and \( \theta \) is the glancing angle.

It is commonly accepted that XRD line broadening may be the result of pure size, or micro strain, or both size and micro strain broadening. Williamson and Hall (W-H) have suggested a method [128] combining the domain size and lattice micro strain effects on line broadening, when both are operative. The W-H approach considers the case when the domain effect and lattice deformation are both simultaneously operative and their combined effects give the final line broadening Full Width Half Maximum (FWHM) (\( \beta \)), which is the sum of \( \beta \) (grain size) and \( \beta \) (lattice distortion). This relation assumes a
negligibly small instrumental contribution compared to the sample-dependent broadening. W-H equation may be expressed in the form

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta$$

(2.2)

where $\varepsilon$ is the strain associated with the nano particles. Eq.2.2 represents a straight line between $4 \sin \theta$ (X-axis) and $\beta \cos \theta$ (Y-axis). The slope of line gives the strain ($\varepsilon$) and intercept ($k\lambda/D$) of this line on Y-axis gives grain size (D).

Fig.2.4 Powder X-ray diffractometer (Shimadzu XRD-7000)

**2.3 FOURIER TRANSFORMATION INFRARED SPECTROSCOPY**

Fourier transformation Infrared (FTIR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply it is the absorption measurement of different IR frequencies by a sample placed in the path of an IR beam.
The main goal of FTIR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. This makes IR spectroscopy as an important and popular tool for compound identification. At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation. FTIR is sensitive to lattice mode thus it is an important and appropriate mode for oxide materials in which lattice parameter plays an important role. The intensities of the FTIR bands provide a good measure of the electronic properties of the oxides. In the present study Perkin Elmer FTIR spectrometer, (spectrum 100) with KBr pellets was used to study the FTIR of as-formed and calcined samples. Solid samples that are difficult to melt or dissolve in any suitable IR-transmitting solvents, pellets are used for the sample (0.5 to 1.0 mg) is finely ground and intimately mixed with approximately 100 mg of dry potassium bromide (KBr) powder. Grinding and mixing is done with an agate mortar and pestle. The mixture is then pressed into a transparent disk in an evacuable die at sufficiently high pressure. Suitable KBr disks or pellets can be made in using a simpler device such as a Mini-Press. To minimize band distortion due to scattering of radiation, the sample is ground to particles of 2 µm (the low end of the
radiation wavelength) or less in size. The IR spectra produced by the pellet technique often exhibits bands at \(3450 \text{ cm}^{-1}\) and \(1640 \text{ cm}^{-1}\) due to absorbed moisture.

Fig. 2.5 FTIR spectrophotometer

2.4 SCANNING ELECTRON MICROSCOPY

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down towards the sample. Accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample.
These signals include secondary electrons (that produce SEM images), back scattered electrons (BSE), diffracted backscattered electrons, photons (characteristic X-rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). Detectors collect these backscattered electrons and secondary electrons to convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.

There is a minor surface charge that influences the clarity of the pictures. Therefore a thin gold coating has to be used to connect the sample surface to the stub for grounding to prevent the accumulation of electrostatic charge on the surface. The scanning electron microscope has many advantages over traditional
microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time.

![Schematic diagram of Scanning electron microscope](image)

Fig. 2.7 Schematic diagram of Scanning electron microscope

As the SEM has higher resolution the closely spaced specimens can be magnified at higher levels. The SEM uses electromagnets rather than lenses so the researcher should have much more control over the degree of magnification. All of these advantages as well as the actual strikingly clear images make the scanning electron microscope one of the most useful instruments in research today.

The prepared samples were analysed using SEM images obtained using a SEM (JSM6390LV; JEOL, Japan) with a magnification from ×5 to ×3, 00,000 to study the morphology of the samples.
**2.5 TRANSMISSION ELECTRON MICROSCOPY**

Transmission electron microscopy (TEM) is used to obtain information from samples which are thin enough to transmit electrons. In TEM the whole area of interest is illuminated simultaneously. An electron source is required to produce large total current so the whole region of interest is illuminated at a useful intensity, even when examining at magnifications of 100x or less. The transmitted electrons are generally used to form either an image or a diffraction pattern of the specimen. The diffraction lens (The lens immediately after the objective lens) are focused on the plane where image is formed by the objective lens. Subsequent lenses are used to magnify this sample further and hence a highly magnified image can be formed on the final screen. In the diffraction lens is focused on the plane where the objective lens forms a diffraction pattern. Again the
lenses below the diffraction are used to magnify further diffraction pattern. There are two different ways of obtaining images of sample in TEM: a) conventional imaging and b) high resolution imaging. First method involves the use of an aperture in the back focal plane, which allows only one electron beam to contribute to the image. This method of obtaining image information excludes the possibility of observing the periodicity of crystalline samples. So the interference of at least two beams is required in the image plane to obtain such periodic information and the contrast arises either from diffraction contrast or phase contrast. The second method of obtaining an image also involves the use of an aperture, but in this case the direct beam and a number of diffracted beams are allowed to contribute to the image. When using the microscope in the conventional image mode, the objective aperture is used to select only one electron beam to form the image. A bright field image is formed indirectly to transmit a selected beam and a dark field image is formed. If the crystal is set up by exciting beam with one strong diffraction, then this beam is selected for imaging. This technique is usually used when crystal defects are imaged. A diffraction pattern is formed in the back focal plane of the objective lens. Hence the diffraction lens is focused onto the back plane of the objective lens, rather than on to the first image plane and when the objective aperture is removed, the diffraction pattern will be visible on final screen. There are two methods which are commonly available a) selected area electron diffraction (SAED) using an aperture
to select the area b) selected area diffraction using a focused electron probe to define the selected area.

The first method is used in conjunction with a defocused electron beam so that a large area of the sample is illuminated with electron and hence this large area is contributing to the generation of diffraction of beams. The technique involves in inserting an aperture in the first image plane so that the electrons generated from the area defined by the aperture will be able to contribute to the diffraction pattern. The other technique is condensing the electron probe to the area of interest, so that the probe positions uniquely define the region where the diffraction beam originates. The electron probe mode is the most common method of obtaining the diffraction pattern. In the present study the Hitachi H-8100 (accelerating voltage up to 200 kV La B6 filament) equipped with an ultrahigh resolution objective pole piece was used in the top entry configuration. The cleaved samples were examined under the transmission electron microscope in order to study the nature of the defect (dislocation) structure and the interplanar spacing. The SAED patterns are also obtained in certain cases. A TEM (CM 200; Philips, USA) was used to obtain sub-structural information and particle size of the prepared samples.
2.6 VIBRATING SAMPLE MAGNETOMETER

The vibrating sample magnetometer (VSM) pioneered by S. Foner, is a simple yet effective technique which is used to characterize the properties of magnetic materials.

VSM uses an induction technique to measure magnetic moment ($\mu$) of a sample. In a VSM the sample is mounted at one end of a rigid rod and then it is kept in oscillating mode in a vertical direction at a fixed frequency. The sample can be magnetized by a horizontal magnetic field and generated by an electromagnet. The sample is covered with a set of sensing coils. As the sample moves its magnetic moment alters the magnetic flux through these coils. The
induced AC voltage is directly proportional to $\mu$ and can be detected using a lock-in amplifier arrangement.

VSM can be used to measure magnetic moment ($\mu$) (> $10^{-4}$ emu), hysteresis loops of ferromagnetic materials, strongly paramagnetic salts and (strongly diamagnetic) superconductors. Based on Faraday’s law of induction, the VSM relies on the detection of the emf induced in a coil of wire which is given by

$$\varepsilon = -N \frac{d}{dt} (BA \cos \theta)$$ (2.3)

where $N$ is the number of wire turns in the coil, $A$ is the coil turn area, and $q$ is the angle between the B field and the direction normal to the coil surface. In practice knowledge of coil parameters such as $N$ and $A$ is unnecessary if the system can be calibrated with a known sample.

A magnetic sample is placed on a long rod and then driven by a mechanical vibrator. The rod is positioned between the pole pieces of an electromagnet, on which detection coils have been mounted. The oscillatory motion of the magnetized sample will induce a voltage in the detection coils. The induced voltage is proportional to the sample’s magnetization and this can be varied by changing the dc magnetic field produced by the electromagnet.

If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins with the field. The stronger the constant field, the larger is the magnetization. The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down,
this magnetic stray field changes as a function of time and this can be sensed by a set of pick-up coils. The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday’s Law of Induction. This current will be proportional to the magnetization of the sample. The greater the magnetization, then greater is the induced current.

The induction current is amplified by a Transimpedance amplifier and lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can tell how much the sample is magnetized and how its magnetization depends on the strength of the constant magnetic field.

Fig. 2.10 Setup of VSM Lakeshore 7410
The VSM consists of the following parts and their importance

- Water cooled electromagnet and power supply
  
  The water cooled electromagnet along with the power supply generates the constant magnetic field which is used to magnetize the sample.

- Vibration exciter and sample holder (with angle indicator)
  
  The sample holder rod is attached to the vibration exciter and the end of it hangs down in between the pole pieces. The exciter moves the sample up and down at a set frequency (~ 85 Hz). The sample rod can be rotated to achieve the desired orientation of the sample to the constant magnetic field. There are also three knobs for controlling the x, y, and z positions of the sample.

- Sensor coils
  
  The sample produces an alternating current in these coils at the same frequency as the vibration of the sample. The signal generated contains the information about the magnetization of the sample.

- Amplifier
  
  The amplifier amplifies the signal created by the sensor coils.

- Control chassis
  
  This controls the 85 Hz oscillation of the exciter.

- Lock in amplifier
  
  This amplifier is tuned to pick up only signals at the vibrating frequency. This eliminates noise from the environment such as from
the overhead lights or hovering spacecraft nearby (unless the noise happens to be an 85Hz signal).

- Computer Interface

The software makes data collection easier by automating the control of the various components during data collection. The data can be graphed and plotted on the printer.

2.7 PHOTOLUMINESCEENCE

When light strikes a phosphor in the ground state it absorbs the radiation of certain specific wavelength to jump to an excited state. A part of the excitation (absorbed) energy is lost on vibration relaxation, i.e., radiation less transition to the lowest vibrational level takes place in the excited state and eventually it returns to the ground state by emitting energy which is called fluorescence. Fluorescence continues for a period of $10^{-8}$ to $10^{-9}$ sec in most cases. Since a part of the radiation absorbed is lost and the fluorescence emitted from the substance has a longer wavelength (lower energy) than the excitation radiation (Stokes’ law).

The emission transition occurring in a solid is seen as a glow and is registered in the form of a band in the luminescence spectrum. The position of the band in the luminescence spectrum does not depend upon the method of excitation. The luminescence spectra are normally observed with the intensity of luminescence as a function of the emission wavelength. The same instrument can be used to measure the spectral distribution of luminescence (emission
Photoluminescence (excitation and emission) spectra were recorded using Shimadzu Spectrofluorometer (Model RF 510) and equipped with 150 W Xenon lamp and Jobinyvon Spectrofluorimeter Fluorolog-3 equipped with 450 W Xenon lamp. Fig. 2.11 depicts the block diagram of the experimental set-up used to record the luminescence spectrum of phosphor sample. The light emitted from the Xe-lamp enters the excitation monochromator. The light emerging from the excitation monochromator is split by the beam splitter and a fraction is directed to the monitor detector. All the driving component i.e., the wavelength drive motors and slit control motors are operated by signal sent from the computer. On the other hand output signal from the monitor detector and fluorescence detector (photomultiplier) are processed by the computer via the A/D converter transmitted to the CRT or graphic plotter.
Fig. 2.11 Block diagram of the photoluminescence spectrometer.

Fig. 2.12 PL instrument used for our studies.