CHAPTER-2

Synthetic and Characterization Techniques
A variety of experimental techniques which are relevant to the present study have been employed to synthesize and characterize new perovskite materials. The aim of this chapter is to give a detailed description of these experimental techniques discussed over here.

2.1 Materials Synthetic Techniques

The synthesis of good quality material is a key to obtain the desired physical properties. Therefore, the selection of sample preparation method is a crucial factor. The increasing interest in developing new materials with interesting properties has stimulated the development of several synthetic techniques in solid state chemistry. Different preparatory methods are used for the fabrication of polycrystalline bulk samples as well as nanosized materials. These include mechanical method such as standard ceramic or solid state reactions method, wet chemical methods include sol-gel based modified Pechini method, combustion process, the nitrate-citrate precursor method etc [1-3]. Each and every method has its own advantages and disadvantages in terms of purity, homogeneity, reactivity and particle size, etc. In the present thesis, following synthetic techniques have been used:

2.1.1 Conventional Solid State Reactions Method

Owing to its simplicity, the conventional solid state reactions method is widely used to synthesize the polycrystalline samples studied during the present work. One of the advantages of the solid state reaction is that the starting materials react without the presence of a solvent. In order to prepare a single-phase sample, the conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure and time for the reaction are needed to be varied according to the phase requirements in the sample [4]. In this method, stoichiometric amounts of commercially available starting materials (usually high purity binary oxides or carbonates of appropriate cations) are accurately weighed out, then mixed thoroughly in an agate mortar and pestle to obtain a homogeneous reaction mixture of particles. Care must be taken to ascertain the correct relative formula mass of these starting precursors and this can be affected by adsorbed species such as water or carbon dioxide, so where necessary precursors are heated to remove these prior to weighing. Volatile solvents such as acetone
or cyclohexane can be used to speed homogenisation. The reaction mixtures are pressed into pellets and then heated in alumina or platinum crucibles at appropriate temperatures with intermediate regrinding-pelletizing until single phase sample is obtained [5]. The sample purity can be readily monitored using X-ray diffraction. After the reaction, the furnace is cooled down to room temperature.

During solid state reactions ceramic synthesis, the phase formation occurs at the interphase between the reacting particles. There are two factors, namely thermodynamic and kinetic, which are important in solid state reaction, the former determines the possibilities of any chemical reaction to occur by the free energy considerations which are involved while the later determines the rate at which the reaction occurs [6,7]. The atoms diffuse through the material to form a stable compound of minimum free energy.

Solids do not usually react together at room temperature over normal time scale so it is mandatory to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate and hence to overcome the slow diffusion rates of the solid materials [4]. Therefore, these reactions depend on diffusion rate of ions towards the grain boundaries. The ions also need sufficient energy to migrate towards these boundaries. The product grains increase in size as the reaction proceeds, hence the rate of the reaction decreases as diffusion path lengths for reacting ions increases. Frequent regrinding between successive heat treatments increases the rate of reaction by creating new interfaces between reactant particles and thus shorter diffusion path lengths [8].

2.1.2 Sol-Gel Technique

A modern technique for nanomaterials synthesis is the sol-gel method, commonly known as sol-gel, or the Pechini method [9]. Sol-gel has become an alternate method to the conventional solid state reactions method, allowing more accurate control over the phase formation, desired stoichiometry and uniformity in particle size. This method involves the mixing of precursors in the liquid phase allows the ions to be mixed at the atomic scale and reduces the problems of lack of homogeneity and slow diffusion rates associated with mixing solid precursors. The ions in solution can then be co-precipitated or converted into a gel (sol-gel method), dried and calcined to obtain the final product. This lowers the sintering temperature and produces small-particle-size materials.
Sol-gel is the cost-effective method, easy to handle and has extensively been used in the synthesis of functional oxides. For nanomaterials synthesis, it is necessary to have control over grain size and also on the phase formation at much lower temperature which can be achieved by using such chemical methods. The pyrolysis of a complex gel seems to be the easiest and the most common variation of the sol-gel methods, which is usually called modified Pechini method as first developed by Maggio Pechini [10], who patented this as a method for forming thin-film capacitors.

The first step involves in this technique is the formation of various metal cation solutions by dissolving the stoichiometric proportions of reactant materials in dilute nitric acid, and resulting solutions are heated at 90°C under constant stirring to ensure the formation of nitrates. Then, solution of dilute citric acid acid (an alpha hydroxyl acid), as a complexation agent and poly ethylene glycol (a polymer of a poly hydroxy alcohol) is added to the mixtures with a careful control of the pH of the solution. The solutions are magnetically stirred on a hot plate at approximately 90°C until a transparent homogenous thick gel is formed. This is decomposed at 300 then 600°C to remove any organic species and the resulting powder calcined at the desired temperature.

In the present work a modified Pechini method, which employs citric acid and ethylene glycol (EG) as a complexing agents was used to synthesize the phases discussed in chapters 4 and 5.

2.1.3 Chemical Combustion Synthesis (CCS)

The physical and chemical properties of nanocrystalline materials depends on the shape and size of nanoparticles. Reduction of the particle size (increasing the surface area) usually results in improved mechanical, electrical and catalytic properties [11,12]. Methods developed to produce small-particle-size materials are many [13] and some of them are complicated and compositional selective or sensitive. However, one of the simplest and today’s widely used method is chemical combustion synthesis for synthesizing the variety of nanosize materials in the nanometric range. The combustion method is very useful and fast process for synthesizing highly homogenous oxides at very low temperatures because no diffusion processes are necessary and hence it is included in
the category of the low-temperature methods for the synthesis of oxides [14].

This process involves initially the mixing of different oxidizers usually metal nitrates in their stoichiometric proportions and combustion fuels (e.g. glycine, urea, polyvinyl alcohol (PVA). The stoichiometry of the redox mixture for combustion is calculated based on the total oxidizing and reducing valencies of oxidizer (O) and fuel (F) so that the equivalence ratio i.e. $\Phi_e (O/F) = 1$ and heat released at its maximum [2]. According to principle of propellant chemistry, the oxidizing and reducing valencies of various elements are taken as: $C = 4$, $H = 1$, $O = -2$, $N = 0$, $M$ (La, Fe and Sr) = 3, 3 and 2 respectively. Thus, total valencies of various metal nitrates $M(\text{NO}_3)_3$ becomes $-15$ and that of $M(\text{NO}_3)_2$ becomes $-10$ which should be balanced by the reducing valencies of organic combustion fuel. Hence, the stoichiometric composition of redox mixture requires $-40 + Fm = 0$, where $F$ stands for total valencies of combustion fuels and $m$ is the moles of fuels in order to release the maximum energy. The mixing at molecular level allows to maintain good chemical homogeneity of the synthesized nanopowders. If a fuel and oxidizer are intimately mixed, burning reaction is self-sustaining, requiring only a small amount of heat to ignite the mass. During combustion, the temperature of the flame can be very high, for a short time, which is sufficient to produce desired nanopowders. Therefore, sufficient heat energy is available for the formation of nanopowders, from the oxidation of the fuel. The availability of such amount of energy and the homogeneity of the precursor solution make their formation easy.

This low-temperature method used in present study to synthesize LaFeO$_3$ and LaSrFeO$_4$ nanopowders (chapters 3 and 6) using different fuels such as PVA, glycine and urea is an attempt to improve their microstructures for various applications.

2.2 Structural Characterization Techniques

2.2.1 Powder X-ray Diffraction (XRD)

Powder X-ray diffraction (XRD) has been used to examine the crystal structure of materials studied in this work. It is one of the most important non-destructive characterization tool nowadays used in solid state chemistry and materials science.
Each crystal structure has its distinctive X-ray diffraction pattern. Once the material has been identified, X-ray diffraction can be used to identify the phase purity, types of phases and crystallographic structure including the crystallographic unit cell, crystal structure, crystallographic texture, crystalline size, macro-stress and microstrain, and also electron radial distribution functions of the powder samples. Fig. 2.1 shows the schematic representation of X-ray diffractometer.

Fig. 2.1: Schematic representation of X-ray diffractometer.

2.2.1.1 Bragg Equation

X-rays are electromagnetic radiations with wavelengths in the order of a few angstroms, which is nearly the same size as the distance between neighbouring atoms that are regularly placed in crystals. When X-rays interact with crystalline materials with a regularly repeating structure, the radiation is scattered from the electron cloud of the atoms in the material. Thus, atoms in a crystal act as scattering centres and thereby diffract X-rays. Diffraction can be constructive or destructive depending on how the
waves overlap one another. Constructive interference occurs when the waves are moving in phase with each other thus, producing very sharply defined points of constructive interference and no signal in the regions where the diffraction condition is not satisfied. This results in diffraction patterns. Destructive interference occurs when the waves are out of phase. Powder diffraction can be understood by considering the Bragg equation.

Depending on the atomic arrangement, interferences between the scattered rays are constructive when the path difference between two diffracted rays differs by an integral number of wavelengths. This detectability condition is described in Fig. 2.2. This selective condition is described by the Bragg equation, also called “Bragg’s law”. In order to observe constructive interference from a specific set of planes, the planes must be correctly oriented relative to the incident X-ray beam. For a crystalline powder sample, a large number of crystallites are present in random orientations so it can be assumed that for any given lattice planes, there will be some crystals oriented with appropriate Bragg angle for constructive interference to occur. Thus, all “Bragg peaks” are measured from the sample as a function of angle $\theta$. A section of a crystal with atoms arrange on a set of parallel planes $(hkl)$, act as scattering centers for X-rays and space a distance $d$ apart is shown in Fig. 2.2. When a beam of monochromatic radiation with wave length $\lambda$ strikes the planes of the crystal at an angle $\theta$, the rays reflected by the lower plane travel a longer distance than those reflected from the upper plane. From the diagram, the path difference between the two beams is the length shown between the two dotted lines. Trigonometrically this length is equal to $2d \sin \theta$, i.e.;

$$AX + BX = 2d \sin \theta$$

In order for constructive interference to occur, this extra distance should be equal to an integral number of wavelengths,

$$n\lambda = AX + BX$$

Therefore,

$$n\lambda = 2d \sin \theta$$
This was first formulated by Bragg known as the Bragg equation [8]. This equation states the essential conditions which must be met if diffraction to occur. The \( n \) in the Bragg equation is known as the order of reflection. In a crystalline material, the atoms are ordered in such a way that a pattern is repeated periodically in three dimensions. The repeating unit of a crystal is known as the unit cell; it contains all the information required to completely reconstruct the structure of the crystal. Fig. 2.3 illustrates the unit cell in a crystalline material.

The unit cell is the smallest unique repeating unit in the structure which exhibits the full symmetry of the material. The lattice parameters \( a, b \) and \( c \) are the unit cell lengths along the \( x, y \) and \( z \) axes respectively. The angles \( \alpha, \beta \) and \( \gamma \) are the angles opposing \( a, b \) and \( c \) in the unit cell. In the lowest symmetry system, \( a \neq b \neq c \) and \( a \neq \beta \neq \gamma \neq 90^\circ \). There are seven different types of possible unit cells, known as crystal systems. These are listed in Table 2.1. All the possible planes of atoms that can cause diffraction events in a crystal are equally spaced and parallel to each other. These lattice planes are described by a set of integers, \((hkl)\), called Miller indices. The Miller indices refer to the reciprocal of the points at which the \( a, b \) and \( c \) axes of the lattice planes are intersected by the plane, denoted \( h, k \) and \( l \) from a defined origin. If a plane is parallel to an axis, then the intercept is infinity which gives a Miller index of zero. Fig. 2.4 shows examples of Miller planes in a crystal.

Knowing that each peak is attributable to one (or more than one equivalent) set of Miller indices it is possible to work back from peak positions to calculate lattice parameters if the crystal symmetry is known or can be worked out. For example, in the case for cubic systems, \( a = b = c, a = \beta = \gamma = 90^\circ \).

Given that; \( \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \) ……… ……… 2.1 and; \( n\lambda = 2d \sin\theta \)

\( \lambda_{hkl} = 2d \sin\theta \) Using \((hkl)\) to define the \( n^{th} \) diffraction plane

\( \lambda^2_{hkl} = 4d^2\sin^2\theta \)………………………………………2.2

\( \frac{\lambda^2_{hkl}}{4a^2} (h^2 + k^2 + l^2) = \sin^2\theta \); substituting 2.1 into 2.2, given that \( a = b = c. \)
Fig. 2.2: Bragg’s law from reflections of incident radiation from successive planes.

Fig. 2.3: The unit cell; (a) stacking a unit cell within a crystal (b) unit cell parameters.
Table 2.1: The seven crystal symmetries, from lowest to highest symmetry.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Lattice parameters</th>
<th>Cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>$V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a = \beta = 90^\circ, \gamma \neq 90^\circ$</td>
<td>$V = abc \sin \beta$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>$V = abc$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a \neq b \neq c$</td>
<td>$V = a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b = c$</td>
<td>$V = a^2 c$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b = c$</td>
<td>$V = \frac{a^2 \sqrt{3}}{2}$</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$V = a^3$</td>
</tr>
</tbody>
</table>

Fig. 2.4: (a) (111), (b) (100), (c) (101) and (d) (10\overline{2}) planes.
So, for a set of reflections it is possible to calculate the cubic lattice parameter from the angle of the diffracted beam. The $2\theta$ peak positions in the X-ray diffraction pattern can be indexed in terms of Miller indices ($hkl$). The Miller indices relate the peak positions or d-spacings to the lattice parameters by an equation specific to the crystal system. Table 2.2 shows the relationship between the d-spacing and Miller indices for the different crystal systems [15].

**Table 2.2:** Relationship between d-spacing ($d_{hkl}$) and Miller indices for each crystal system, these equations are also used to index non-cubic diffraction peaks.

<table>
<thead>
<tr>
<th>Crystal symmetry</th>
<th>Relationship between d-spacing ($d_{hkl}$) and Miller indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left[ \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hlcos\beta}{ac} \right]$</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{d^2} = \frac{1}{\sqrt{V}} \left[ h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma \right.$</td>
</tr>
<tr>
<td></td>
<td>$+ 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$</td>
</tr>
<tr>
<td></td>
<td>$+ 2klbca^2(\cos\beta\cos\gamma - \cos \alpha) + 2hlacb^2(\cos\alpha\cos\gamma - \cos \beta)$</td>
</tr>
<tr>
<td></td>
<td>$V = abc\sqrt{[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]}$</td>
</tr>
</tbody>
</table>

| Triclinic            | $\frac{1}{d^2} = \frac{1}{\sqrt{V}} \left[ h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma \right.$ |
|                      | $+ 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$                                                                               |
|                      | $+ 2klbca^2(\cos\beta\cos\gamma - \cos \alpha) + 2hlacb^2(\cos\alpha\cos\gamma - \cos \beta)$                              |
|                      | $V = abc\sqrt{[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]}$                         |
2.2.1.2 Crystallite Size \((D)\)

By examining the peak positions in a diffraction pattern, the size and shape of the unit cell can be determined. The relative intensities of the peaks provide information about the arrangement and types of atoms within the unit cell, while analysis of the peak widths can give the crystallite size of the material studied. The size of the crystals can affect the width of the peaks in a diffraction pattern if the crystals themselves or ordered domains within a large particle are small. Small crystals can therefore cause broadening and this allows powder XRD to be used for estimating crystallite sizes. The relationship between crystallite size and the peak width is determined by the Scherrer equation \([16]\);

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \(D\) is the mean crystallite size, \(K\) is a constant \((0.9)\), \(\lambda\) is the X-ray wavelength used, \(\beta\) is the full width at half maximum (FWHM) of a peak in radians and \(\theta\) is the peak position. The peak width also depends on instrumental broadening. This effect can be corrected by subtracting the FWHM of a standard reference sample with negligible size broadening, \(\beta_i\), from the measured sample, \(\beta_s\).

\[
\beta^2 = \beta_s^2 - \beta_i^2
\]

where \(\beta_s\) is FWHM for sample measured, \(\beta_i\) is FWHM due to instrumental resolution.

2.2.1.3 Generation of X-rays

X-rays used for X-ray diffraction (XRD) can be generated in many ways. The most commonly used method, the X-ray tube method, is introduced here. The X-ray tube method is actually Röntgen’s method and is mostly used in laboratory X-ray diffractometers. In this method, X-rays are produced by the continuous bombardment of a metal anode with high energy electrons produced by thermionic emission of a tungsten filament. The electron source, a filament, is heated to produce electrons which are then accelerated in vacuum by a high electric field in the range 20-60 kV and hit a metal target (anode), Cu in the current study, producing both continuous and characteristic X-rays \([\text{Fig. 2.5(a)}]\).
The characteristic Cu X-rays have wavelengths $K\alpha_1 = 1.5406\text{Å}$, $K\alpha_2 = 1.5444\text{Å}$, $K\beta_{1,3} = 1.3922$ and $K\beta_3 = 1.3926\text{Å}$ in an approximate intensity ratio of 100:50:30:15 [17]. Since the wavelengths of the two $K\beta$ lines are very close, they are generally treated as one wavelength described as $K\beta$, [Fig. 2.5(b)] [18]. In X-ray diffraction, monochromatic radiation (single wavelength) is required, usually $K\alpha_1$, the most intense of the characteristic X-rays, is selected. In an XRD pattern, $K\beta$ and $K\alpha_2$ will cause extra peaks, and shape changes. They should be eliminated by adding filters. $K\beta$ lines can be filtered out using a filter made of a thin metal foil of the element with one atomic number smaller than the X-ray source element, such as Ni filter for Cu radiation. Removal of the $K\alpha_2$ line is not as simple. Most of the conventional (laboratory) X-ray diffractometers, including that used in this work are not monochromatic and contain $K\alpha_1+K\alpha_2$ lines.

In the present work, powder X-ray diffraction data were collected at room temperature by using powder X-ray diffractometer (PANanalytical X’PertPRO MRD, Netherlands, equipped with Ni-filtered CuK$\alpha$ radiations) operated at 45 kV and 40 mA. A photograph of the PANanalytical X-ray diffractometer is shown in Fig. 2.6. For monitoring phase purity, finely ground samples were placed in sample holders with silicon sample plates, and pressed with glass slides to obtain a flat sample surface, (Fig. 2.6). Good quality diffraction data for structure refinement is typically collected over the full range possible with the detector, in the $2\theta$ scanning range from 20° to 100° with a step size of 0.0171° and continuous scan step time of 21s. The refinement was carried out by means of the program GSAS (General Structure Analysis System) [19].

2.2.1.4 Intensities of X-ray Reflections

Intensities of X-ray reflections are important in determining unknown crystal structures and characterising materials. The intensity $I_{hkl}$ for each reflection is given by;

$$I_{hkl} = K \times p_{hkl} \times L_\theta \times P_\theta \times A_\theta \times T_{hkl} \times E_{hkl} \times F^2_{hkl}$$

where $K$ is the scale factor, $p_{hkl}$ is the multiplicity factor which accounts for the number of equivalent reflections that contribute to an observed Bragg peak, $L_\theta$ the Lorentz factor is a geometric factor that depends on the type of instrument and varies with $\theta$, $P_\theta$ the polarisation factor accounts for the angular dependence of intensity scattered by
**Fig. 2.5:** (a) X-ray production on a conventional X-ray tube, and (b) Cu X-ray emission spectra.

**Fig. 2.6:** Set up of the PANalytical X-ray diffractometer used for monitoring phase purity.
electrons, \( A_\theta \) is the absorption factor, \( T_{hkl} \) is the preferred orientation factor, \( E_{hkl} \) is the extinction multiplier and \( F_{hkl} \) is the structure factor. The absorption factor accounts for the reduction in the intensity of the diffracted X-ray beam due to absorption by the sample.

The structure factor for a peak \((hkl)\), \( F_{hkl} \), the resultant of the waves scattered by \( n \) number of atoms in the unit cell is given by the equation;

\[
F_{hkl} = \sum_{j=1}^{n} g_j t_j(s) f_j(s) \exp \left[ 2\pi i (hx_j + ky_j + kz_j) \right]
\]

where \( g_j \) is the population factor of the \( j^{th} \) atom, \( t_j \) the atomic displacement parameter of the \( j^{th} \) atom, \( f_i \) is the scattering factor, \( x_j \), \( y_j \) and \( z_j \) are the fractional coordinates of the \( j^{th} \) atom \([20]\). Thermal vibrations of atoms decrease intensities of diffracted beams and increase background scatter \([18]\). The atomic displacement parameter \( t_j \) of the \( j^{th} \) atom also known as the temperature factor describes the influence of the motions of atoms and is given by;

\[
t_j = \exp \left[ -B_j \frac{\sin^2 \theta}{\lambda^2} \right]
\]

where \( B_j \) is the isotropic displacement parameter for the \( j^{th} \) atom and this can be related to the vibration of the \( j^{th} \) atom by;

\[
B_j = 8\pi^2 U_j
\]

where \( U_j \) is the mean square amplitude of vibration of the atom in \( \text{Å}^2 \) \([21]\).

X-rays are scattered by crystalline material due to their interaction with the electrons in the material. This is described by the scattering factor \( f_n \) which depends on the atomic number \( Z \) or rather on the number of electrons present in the atom. Due to this dependence scattering from heavy atoms can dominate X-ray diffraction patterns and it can be difficult to obtain reliable information on light atoms from X-ray diffraction data. X-rays scattered from different parts of the atom can interfere destructively due to the relatively diffuse nature of the electron cloud. This gives rise to a significant decrease in
scattered intensity with increasing angle as the scattering factor $f_n$ decreases from a value of $Z$ at $2\theta = 0$. This can result in a loss of information from the high angle region of XRD patterns.

2.2.1.5 Rietveld Refinement

The Rietveld refinement method is a widely used tool for the structural characterization of polycrystalline materials. Rietveld pioneered the technique, now used by solid state chemists, to fit a modeled diffraction pattern to a whole data set [19]. The refinement process uses a well-established mathematical procedure called a whole pattern least square analysis [22], which aims for a ‘best fit’ of data by minimising the difference between all of the observed intensity points (experimental data) and the calculated intensities (model data). The technique therefore, requires powder X-ray diffraction data file where intensities of the scattered radiations have been recorded as increments of Bragg angle $2\theta$ at well defined steps and a model structure. To achieve this certain variables are adjusted, which are related to the crystal structure, such as lattice parameters, atomic coordinates, thermal parameters and site occupancies. Instrumental parameters such as wavelength and profile parameters that describe peak shapes are also refined. Both instrumental factors such as radiation source and sample effects such as crystallite size, stress and strain contribute to the peak shape. Thus, peak shape should be well fitted. The peak shapes in powder X-ray diffraction data are described as a combination of Lorentzian and Gaussian functions, modelled by a pseudo-Voigt function while constant wave length neutron powder diffraction commonly produces Gaussian peaks [23].

In present work, Rietveld profile refinements were performed on the XRD data using the the software package GSAS [19]. The aim of structural refinement is to minimise the difference between the calculated diffraction pattern and the observed pattern recorded from the phase of interest. The intensity of the diffracted beam, $I_{hkl}$ is proportional to the structure factor, $F_{hkl}$ by the relationship defined as:

$$I_{hkl} \propto |F_{hkl}|^2$$
A good starting model for crystal structure including the space group, approximate lattice parameters and position coordinates is required for the Rietveld method in order to obtain the global minimum and not a local minimum. The quantity minimised in the least squares refinement is the residual $S_y$ [24];

$$ S_y = \sum_i \left\{ w_i \left( y_i(\text{obs}) - y_i(\text{calc}) \right) \right\}^2 $$

where $w_i$ is the weighting factor assigned to the individual step intensity, usually taken as; $w_i = 1/y_i(\text{obs})$, $y_i(\text{obs})$ is the set of observed diffraction intensities collected at the $i^{th}$ step across the pattern, $y_i(\text{calc})$ is the set of corresponding calculated values. The agreement between the observed and calculated model is quantitatively indicated by several reliability or $R$-factors. The weighted profile residual ($R_{wp}$), the profile residual ($R_p$), the Bragg residual ($R_B$), the expected profile residual ($R_{exp}$) and the value of ($\chi^2$) is used to describe the “goodness of fit” ($GOF$) of the overall refinement [25].

The equations below describe these different parameters:

$$ R_{wp} = \left\{ \frac{\sum w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum w_i y_i(\text{obs})^2} \right\}^{1/2} $$

$$ R_p = \frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})} $$

$$ R_B = \frac{\sum |I_k(\text{obs}) - I_k(\text{calc})|}{\sum I_k(\text{obs})} $$

$$ R_{exp} = \left\{ \frac{(n - p + c)}{\sum w_i y_i(\text{obs})^2} \right\}^{1/2} $$

where $I_k(\text{obs})$ is the ‘observed’ integrated intensity of reflection $k$ calculated at the end of the refinement after apportioning each $y_i(\text{obs})$ between the contributing peaks according to the calculated intensities $I_k(\text{calc})$, $n$ is the number of observations, $p$ the number of refinable parameters and $c$ the number of constraints applied.
\[(GOF) = \chi^2 = \frac{R_{wp}}{R_{exp}}\]

The expected profile residual \(R_{exp}\) value gives an idea of how well the data could be modelled, based on the number of parameters and the number of steps in the pattern. The weighted profile residual \(R_{wp}\) and the profile residual \(R_{p}\) are based on summing the difference between the observed and calculated data at each step in the pattern; in the case of \(R_{wp}\), the numerator is the residual being minimised in the least squares procedure. \(R_{wp}\) is weighted according to the observed intensity of each step, so that a greater absolute difference between observed and calculated intensities is allowed where the observed intensity is high. The \(GOF\) is defined as the ratio of \(R_{wp}\) and \(R_{exp}\); a value of \(\chi^2 = 1\) would describe a perfect fit. The Bragg residual \(R_B\) value is concerned only with how well the Bragg peaks have been modelled, and can be useful in fitting patterns that contain peaks not belonging to the phase(s) being modelled.

### 2.3 Oxygen Content Analysis

Rietveld refinement of the XRD data can be used to roughly establish the oxygen content of the perovskite oxides and related compounds based on the values obtained for the oxygen occupancy at different structural sites. However, the sensitivity of XRD for oxygen is low and the obtained occupancy values are seldom precise, resulting in large errors in the resultant oxygen content values. More precise results can be obtained by employing either synchrotron X-ray or neutron sources, but these methods are expensive and available measurement time is limited. Therefore, the wet-chemical redox titrations such as iodoetric and cerimetric titrations are commonly used for the analysis of exact oxygen content in the perovskite oxides and related compounds [26-29].

However, as these methods can provide only average oxygen content of the phase, they work best when used in conjunction with site-specific methods such as Rietveld refinement. With the combination of chemical and site-specific methods, it becomes possible to precisely determine the oxygen vacancy concentration and oxidation state of transition metal cations on each structural sub-unit. Iodometric titration is probably the most widely used wet chemical method for the oxygen content analysis of transition
metal oxides [26]. It is based on the reduction of high-valent ions in an acidic solution by KI, which reduces transition metal ions to their low-valent iodides. Iodine formed in the reactions is titrated by a sodium thiosulphate solution using starch as an indicator. From the volume of sodium thiosulphate solution, which is used to titrate, the amount of liberated iodine is determined. The average transition metal oxidation state or oxygen content in the samples can then be calculated from the obtained amount of iodine with an accuracy of ±0.002. Iodometric titration is suitable for oxides of iron, cobalt, copper and/or manganese [30-35]. In the cerimetric titration the high-valent ions of iron or cobalt are reduced by a known excess of Fe$^{2+}$ ions and unreacted Fe$^{2+}$ ions are titrated by a cerium sulphate solution using ferroin as an indicator [36,37]. In present work, oxygen content analysis was done using both cerimetric and iodometric titrations.

2.4 Composition and Microstructure Analysis

2.4.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Scanning Electron Microscopy (SEM) is a powerful magnification tool that utilizes focused beams of electrons to obtain high-resolution magnified images for studying the texture, topographical and morphological information. In SEM analysis, an electron beam, which typically has an energy ranging from 0.2 to 40 keV, is focused on the sample and interacts with the atoms. Two types of X-rays result from these interactions; background X-rays (or continuum), and element specific characteristic X-rays. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

Accelerated electrons in SEM analysis carry significant amount 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), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals, photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light 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. Characteristic X-rays are produced for each element in a mineral that is ‘excited’ by the electron beam. SEM analysis is considered to be ‘non-destructive’; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. The schematic block diagram of SEM is shown in Fig. 2.7 indicating the interaction of the electron beam with a sample producing secondary, reflected electrons, X-rays, etc. Depending on the type of the detector, the radiation emitted by the sample is transformed into electrical signals which, after amplification, are used to modulate a cathode-ray tube display where an image of the sample surface is formed.

In present work, three different SEM instruments were used to identify the morphology of the materials. These are (FE-SEM Quanta 200 FEG with accelerating voltage 200V–30 kV), SEM, JEOL-JSM 6610LV with accelerating voltage between 0.3–20 kV and Field Emision Scanning Electron Microscope (FE-SEM) Carl Zeiss Ultra Plus with resolution upto 0.8nm. The SEM instruments are equipped with Energy Dispersive X-ray analysis (EDX) detectors which can also provide compositional information for a selected region in the SEM image. EDX is a qualitative and quantitative X-ray micro-analytical technique that can provide information on the chemical composition of a powder sample for its elemental analysis. Its characterization abilities are due in large part to the basic principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified. The X-rays are detected by an Energy Dispersive detector which displays the signal as a spectrum, or histogram, of intensity (number of X-rays or X-ray count rate) versus energy. The elemental ratios can be determined from the EDX analysis and therefore this data can be used to examine the doping level, compositional percentage of a given sample area.
Fig. 2.7: Schematic block diagram of a Scanning Electron Microscopy in operation.
2.4.2 Transmission Electron Microscopy (TEM)

For the same reason as for neutrons and X-rays, electrons can also be used for diffraction. Transmission Electron Microscopy (TEM) uses electrons generated by an electron gun for diffraction studies of materials. Based on the de Broglie equation, \( \lambda = \frac{h}{mv} \) and the kinetic energy \( E = \frac{mv^2}{2} \), the electron wavelength is;

\[
\lambda = \frac{h}{\sqrt{2mE}}
\]

Thus, wavelength \( \lambda \) is related to the energy of electrons \( E \) in the unit of accelerating voltage, eV. If an electron beam has high enough energy then a diffraction pattern of the crystal structure can be obtained.

By analogy to an optical microscopy, which lets us observe the interaction of matter with light, a TEM allows us to see the interaction of matter with electrons. The typical setup of a TEM is shown schematically in Fig. 2.8. The principle of a TEM experiment can be described as follows: the electron gun (typically made of LaB\(_6\)) generates an electron beam that is focused by the condenser lenses. After that, the beam interacts with the specimen and passes through it. The transmitted and diffracted electrons are then recombined and focused by the objective lens to form a diffraction pattern and an intermediate image at the back focal plane. The beams then diverge and are focused by the projector lens to form the final image. Whether an electron diffraction pattern and an image is achieved is determined by choosing images from the back focal plane or the image plane. Resolution down to less than 2Å can be achieved. TEM offers two methods of specimen observation, diffraction mode and image mode. In diffraction mode, an electron diffraction pattern is obtained on the fluorescent screen, originating from the sample area illuminated by the electron beam.

The diffraction pattern is entirely equivalent to an X-ray diffraction pattern: a single crystal will produce a spot pattern on the screen and a polycrystal will produce a powder or ring pattern. In image mode, the post-specimen lenses are set to examine the information in the transmitted signal at the image plane of the objective lens. Here, the scattered electron waves finally recombine, forming an image with recognizable details related to the sample microstructure (or atomic structure).
Fig. 2.8: Operation modes of a typical TEM analysis: (a) diffraction, (b) imaging.
In present work, TEM measurements were performed on Hitachi-7500 electron microscope (Japan), operating at an acceleration voltage of 120 kV, TEM CM 200 with operating voltage 20-200kV and (TEM, Model; Technai G2 20 S-TWIN FEI Netherlands, with an accelerating voltage of 20-200 kV). Samples for TEM analysis were prepared by placing a drop of the powder sample suspension after treated with oscillation thoroughly on a carbon-coated copper TEM grid, allowing it to dry in air and then analyzed.

2.5 Density Measurements and Porosity

The bulk density of the sintered pellets of the samples was determined by Archimedes’ method with n-butanol, which is given by the relation

\[
\frac{\text{Density of sample}}{\text{Density of fluid (n-Butanol)}} = \frac{\text{Weight of pellet in air}}{\text{Weight of pellet in air – apparent immersed weight}}
\]

The percentage porosity of the sample was calculated using the relation [38]:

\[
P = \left[1 - \left(\frac{d_{\text{mea}}}{d_{\text{cal}}}\right)\right] \times 100
\]

where \(d_{\text{mea}}\) is the measured density and \(d_{\text{cal}}\) is the X-ray density.

2.6 Magnetic Susceptibility and Magnetization Measurements

A number of techniques are used for the determination of magnetic susceptibility [39]. One of such techniques known as constant force method or non-uniform field method, also known as Faraday magnetic balance method, is a sensitive and accurate method used for the magnetic susceptibility measurements. A cartoon of the experimental setup is represented in Fig. 2.9. It is comprised of a thread made from a diamagnetic material and electromagnets with iron cores shaped as Faraday pole caps. Specially fabricated Dewar flask of the size which could be adjusted within the pole gaps of the electromagnets was used for keeping liquid nitrogen, which surrounded the sample crucible. The sample is freely suspended between the iron cores in a quartz made crucible attached to the thread.
Fig. 2.9: Schematic diagram of the Faraday magnetic apparatus.
A magnetic force is applied to the powder sample by the field gradient \((dH/dZ)\) created between the Faraday pole caps. The force depends only on the total mass of the material present and is measured as a weight change, using a magnetic balance. The displacement \((Z)\) of the sample along the vertical axis above the central line of the pole gaps corresponding to a new equilibrium between the thread’s recoil and the magnetic force is then used to infer the susceptibility. This has two unknowns; the sample’s susceptibility and the product \(H.dH/dz\). This condition is met in the Faraday method by using specially designed pole faces (Fig. 2.9) This results in a vertical force applied to the sample, which is expressed by the relation:

\[
F = m\chi H \left( \frac{dH}{dZ} \right)
\]

where \(F\) is the force in dynes, \(m\) is the mass of sample in grams and \(\chi\) is the susceptibility per gram, \(H\) the field generated by the electromagnet and \(dH/dz\) the Field gradient along the vertical axis and \(z\) the vertical displacement.

Experimentally, the magnetic susceptibility of the powder sample is measured as a function of temperature in the temperature range from 80 to 300 K. Both zero-field-cooled (ZFC) and field-cooled (FC) measurements are carried out and the data is collected upon warming after cooling the sample in the absence of a magnetic field (ZFC) and after cooling in the presence of a magnetic field (FC). The data obtained is then corrected for diamagnetic interactions using Pascal constants and then used to describe the magnetic interactions occurring inside the material. The gram magnetic susceptibility \((\chi_g)\) of synthesized samples may be calculated from the following equation;

\[
\chi_g = (\chi_g)_s \left( \frac{w_s}{w_c} \right) \left( \frac{\Delta w_c}{w_c} \right)
\]

where \(\chi_g\) is the gram susceptibility of compound, \((\chi_g)_s\) is gram susceptibility of standard sample \((16.44 \times 10^{-6} \text{ cgs units at } 20\degree C)\), and \(w_s\) is the weight of the standard sample in the absence of magnetic field, \(w_c\) denotes the weight of the compound in the absence of magnetic field, \(\Delta w_s\) the change in weight of the standard sample after the applied magnetic field, and \(\Delta w_c\) the change in weight of the compound after the applied magnetic
field. The molar magnetic susceptibility ($\chi_m$) values were then calculated from the gram magnetic susceptibility values using the following equation

$$\chi_m = \chi_g \times \text{Molecular Weight}$$

The effective magnetic moment of the samples can be calculated from the molar magnetic susceptibility using the following equation

$$\mu_{eff} = 2.828 \sqrt{\chi_m T}$$

where $\mu_{eff}$ stands for effective magnetic moment in Bohr magnetons (B.M.) and $T$ is the absolute temperature.

One of the advantages of the Faraday method is that a very small amount of sample (usually in milligrams) is required for experiment and the temperature control of sample is considerably easier during measurement of magnetic susceptibility. In order to determine the field and its variation, the Faraday Balance was calibrated prior to use with standard reference sample of Mercury(II)tetrathiocyanatocobaltate(II), Hg[Co(SCN)$_4$], a molecular paramagnet of known susceptibility.

### 2.7 Electrical Resistivity Measurements

Electrical resistivity measurements of the polycrystalline materials as a function of temperature are rather easy and straightforward to make and provide much useful information about the various temperature dependent electronic phase transitions. It also provide us an easily accessible and accurate value of the critical temperature as well as information of the quality of the sample. A low contact resistance is desirable due to the small resistance of the samples. To fulfill this requirement, standard four-probe technique is used for measuring resistivity of the powder samples in the present study [40]. The samples are first cooled down to their superconducting state by using liquefied nitrogen and then heated in a controlled way by using a heating oven and resistivity is measured with slowly warming process.

To measure the resistivity using this technique, the powder samples are first ball milled and pelletized by uniaxial pressing by hydraulic press and then sintered at high
temperatures to give densities higher than 90% of their theoretical densities. For the electrical contacts of the probes with the sample silver paste or silver epoxy has been used. This silver paste is applied on the surface of the pellet at the ends for current and voltage contacts. Due to very less resistance, thin copper wires are connected with silver paste or silver epoxy.

The low resistance of the samples, between 50 and 200 mΩ at room temperature requires sensitive instruments. Therefore, a precise accurate current source, which can pass current of microamperes to a few nanoamperes and a digital voltmeter have a measurable range from microvolts to a few volts is preferable. As shown in the Fig. 2.10, constant current is passed through the outer probes \((I^+ \& I^-)\) and resultant potential difference developed between two points is measured using the inner probes \((V^+ \& V^-)\). The gap between all the four probes is fixed and equal in the whole arrangement. The resistance can be calculated using the ohm’s law \(V = IR\), where \(I\) is the current passed and \(V\) is the voltage developed. It is imperative to keep the voltage probes between the current probes in a linear way. Using dimensions, shown in Fig. 2.10 and the dimensions of the pellet, the exact resistivity \((\rho_o)\) of the sample can be calculated using the relation;

\[
\rho_o = \frac{V}{I} \times 2\pi s
\]

where \(s\) is the distance between the probes. A correction factor \(G\), which is a function of the thickness \((t)\) of the pellet and probe distance, has been applied to the relationship. After application of the correction factor, the specific resistance is given by the relation;

\[
\rho = \frac{\rho_o}{G}
\]
Fig. 2.10: Collinear four-probe array on the surface of a spherical pellet having thickness (t); outer probes 1 and 4 are the current (I) input and output probes; inner probes 2 and 3 measure the potential difference, (V) between them.
References


507.


