This chapter presents a brief background of the various methods of sample preparation and characterization techniques used for studying properties (like structural, electric dielectric, and magnetic) of Cr and Mn substituted lithium ferrite. The details of experimental techniques, various characterization equipments and their working details are also given in this chapter.

3.1 Synthesis method

Sol gel method is an important mean of preparing inorganic oxides. It is a wet chemical method and a multistep process involving both chemical and physical processes. A sudden increase in viscosity is the common feature in sol-gel processing, indicating the onset of gel formation. The important features of the sol-gel method are.

a) Better homogeneity

b) High purity
c) Lower processing temperature
d) Better size and morphological control
d) More uniform phase distribution in multi component systems like ferrites.

The steps in sol gel synthesis are as follows.
i) **Hydrolysis:** The process of hydrolysis may start with a mixture of metal alkoxide and water in a solvent usually alcohol at the ambient or slightly elevated temperature.

ii) **Polymerization:** This step involves condensation of adjacent molecules where in H\(_2\)O and alcohol are eliminated and metal oxide linkages are formed. Polymeric networks grow to colloidal dimensions in the liquid (sol) state.

iii) **Gelation:** In this step, the polymeric networks link up to form a threedimensional network throughout the liquid. The system becomes somewhat rigid, on removing the solvent from the sol. Solvent as well as water and alcohol molecules remain inside the pores of the gel.

iv) **Drying:** Water and alcohol are removed at moderate temperatures leaving a hydroxylated metal oxide with residual organic content.

V) **Dehydration:** This step is carried out between 670 K and 1070 K to take off the organic residues and chemically bound water, yielding a glass metal oxide.
VI) **Densification:** Temperature in excess of 1270K are used to form the dense oxide product. The sol-gel technique has been used to prepare sub micrometer metal oxide powders with a narrow particle size distribution and unique particle shapes. Metal-ceramic composites as well as organic-inorganic composites have been prepared by the sol gel route. Fig. 3.1 depicts the flow chart of sol-gel auto-combustion method.

![Flow chart of sol-gel auto-combustion method](image)

**Fig. 3.1: Flow chart of sol-gel auto-combustion method**
3.2 Characterization techniques

3.2.1 X-ray diffraction

The X-ray diffraction technique is used for the structural/phase analysis of the material under investigation. The basic principle is that for a fixed wavelength (λ), the constructive interference occurs for a fixed set of an interplaner spacing (d) and incidence angle (θ) (Figs. 3.2 & 3.3). According to Bragg’s condition of diffraction:

\[ n\lambda = 2dsin\theta \quad 3.1 \]

For cubic system, d is given by

\[ \frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad 3.2 \]

Combining the above two equations we get a relation, which predict the diffraction angle for any set of planes for a given ‘λ’ if the following condition is satisfied,

\[ Sin^2\theta = \frac{2}{4a^2}(h^2 + k^2 + l^2) \quad 3.3 \]

Fig. 3.2: Basic principle involved in diffraction of X-ray beam from assembly of lattice-atoms
It is seen that diffraction directions are determined by the shape and size of the unit cell. This is an important point. All we can possibly determine about an unknown crystal by the measurement of the directions of diffracted beams are the shape and size of its unit cell. The intensities of diffracted beams are determined by the positions of the atoms within the unit cell and it follows that we must measure intensities if we are to obtain any information about the atom positions. It is also found for many crystals, that there are particular atomic arrangements, which reduce the intensities of some diffracted beams to zero. In such cases, there is simply no diffracted beam at the angle predicated by the equations of the type eqs. (3.3 and 3.4). It is in this sense that equations of this kind predict all possible diffracted beams.

Fig. 3.3: Schematic diagram of Bragg’s diffraction

While indexing for cubic structure, it has to be kept in mind that for simple cubic and simple tetragonal all \((h k l)\) values are permissible,
yet reflections corresponding to \((h^2+k^2+l^2)\) values equal to 7, 15, 23.... are all absent. The reflection peaks for bcc satisfy the condition \(h+k+l = 2n\).

For fcc structure, the reflection peaks are found to have \((h k l)\) values either all even or all odd. The average grain size of the sample can be calculated from the width of the peak by using the relation:

\[
t = \frac{K\lambda}{B\cos\theta}
\]  

where \(B\) is the broadening of line expressed in the unit of \(2\theta\), \(K\) is a constant \(\sim 1\) in most case and \(t\) is the average length of the crystallites; and \(\lambda\) and \(\theta\) have their usual meanings.

Generally, X-ray diffraction provides information about the:

(a) Long range order structure  
(b) Phase composition  
(c) Crystallinity, crystal size and shape  
(d) Micro-stress and strain  
(e) Texture (crystal orientation)

X-ray diffraction technique is a powerful technique to study the crystal structure of a material. Qualitatively and quantitatively it also determines the amorphous contain of the sample. The technique helps in identifying the constituents of multiphase mixture. The X-ray diffraction pattern yields information of the position of Bragg’s peaks. The XRD patterns also helps to identify the structural phases present in the end product obtain by the method of preparation used. The XRD patterns of
all the samples were recorded on Philips X-ray diffractometer (Model 3710) by employing the following specification.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target:</td>
<td>Cu-Kα</td>
</tr>
<tr>
<td>2θ range:</td>
<td>20-80°</td>
</tr>
<tr>
<td>Step width:</td>
<td>0.02</td>
</tr>
<tr>
<td>Count rate:</td>
<td>400-700 counts/sec.</td>
</tr>
</tbody>
</table>

3.2.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-
resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.
Fig. 3.4: Schematic diagram of an SEM.

Scanning process and image formation

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB$_6$) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide.
The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the $x$ and $y$ axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron’s landing energy, the atomic number of the specimen and the specimen’s density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is
therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

**Magnification**

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.
Sample preparation for SEM

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation.

Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z). The
improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

An alternative to coating for some biological samples is to increase the bulk conductivity of the material by impregnation with osmium using variants of the OTO staining method (O-osmium, T-thiocarbohydrazide, O-osmium). Nonconducting specimens may be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or field emission gun (FEG) SEMs operated at low voltage. Environmental SEM instruments place the specimen in a relatively high pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high pressure region around the sample in the ESEM neutralizes charge and provides an amplification of the secondary electron signal. Low voltage SEM of non-conducting specimens can be operationally difficult to accomplish in a conventional SEM and is typically a research application for specimens that are sensitive to the process of applying conductive coatings. Low-voltage SEM is typically conducted in an FEG-SEM because the FEG is capable of producing high primary electron brightness even at low accelerating potentials. Operating conditions must be adjusted such that the local space charge is at or near neutral with adequate low voltage secondary electrons being
available to neutralize any positively charged surface sites. This requires that the primary electron beam's potential and current be tuned to the characteristics of the sample specimen.

Embedding in a resin with further polishing to a mirror-like finish can be used for both biological and materials specimens when imaging in backscattered electrons or when doing quantitative X-ray microanalysis [1].

**Materials evaluation by SEM**

- Grain size
- Surface roughness
- Porosity
- Particle size distributions
- Material homogeneity
- Intermetallic distribution and diffusion

### 3.2.3 **Infrared Spectroscopy (IR)**

Infrared spectroscopy is the method of choice of qualitative analysis of organic material and it has wide application to inorganic substances as well. The infrared spectrum of a material has aptitude for the fingerprint, a unique property of that material and of its physical state. The spectrum is unique because it reflects the vibration between
atoms within the molecule, and even slight changes in geometry or bond strength between atoms cause noticeable shift in the infrared absorption pattern.

When a molecule interacts with the radiation of the proper frequency, it absorbs energy and molecule is set into vibration. By measuring the transmitted energy as a function of radiation frequency, we can determine which frequency has been absorbed by the sample. The resulting plots of energy versus frequency are the infrared spectrum of the sample.

The infrared spectra of all the samples of the present series were recorded at room temperature in the range 400 cm\(^{-1}\)-800 cm\(^{-1}\) on a Perkin Elemer spectrometer (Model 783). To study the I.R. spectra of all the samples, about one gram of fine powder of each sample was mixed with KBr in the ratio 1:250 by weight to ensure uniform distribution in the KBr pellet. The mixed powder was then pressed in a cylindrical die to obtain clean disc of approximately 1 mm thickness. The IR spectra were used to locate the band position. The IR spectra were used to determine bond length \(R_A\) and \(R_B\), in a cubic crystal for tetrahedral (A) and octahedral [B] site using formula given by Gorter [2]. Using the analysis of Waldron [3], the force constant \(K_0\) and \(K_i\) were calculated.
3.2.4 Vibrating Sample Magnetometer (VSM)

A vibrating sample magnetometer or VSM is a scientific instrument that measures magnetic properties invented in 1955 by Simon Foner at Lincoln Laboratory MIT. The paper about his work was published shortly afterward in 1959 [4]. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear actuators of some form and historically the development of these systems was done using modified audio speakers, though this approach was dropped due to the interference through the in-phase magnetic noise produced, as the magnetic flux through a nearby pickup coil varies sinusoidally. The induced voltage in the pickup coil is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.

A typical hysteresis curve of a spinel ferrite is also shown in Fig. 3.5. A great deal of information can be learned about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the
relationship between the induced magnetic flux density ($B$) and the magnetizing force ($H$). It is often referred to as the B-H or M-H loop.

**Fig. 3.5: A typical hysteresis curve of a spinel ferrite.**

From the hysteresis loop, a number of primary magnetic properties of a material can be determined such as magnetization ($M_s$), coercivity ($H_c$), remanence magnetization ($M_r$) etc.

### 3.2.5 DC Resistivity

The compositional and temperature dependence of electrical resistivity of the present samples has been studied by two probe technique. The samples in disc shaped form are held in between two electrodes of a sample holder.
A specially designed sample holder was used to measure the resistivity. To make parallel smooth faces of the pellets they were rubbed with zero grade ambary grade paper and graphite rod. A thin layer of silver paste was applied on both the flat surface of the pellets for good electrical contact.

The sample holder along with the sample is placed in an electric furnace. The temperature of the furnace was varied using dimmer. A suitable thermocouple (Chromel- Alumel) was used to measure the temperature of the sample. The resistance of a sample was measured at the regular interval of temperature (10K).

The values of resistivity were calculated using the following equation,

$$\rho = \frac{R \cdot A}{l}$$

where, A is cross-sectional area of the pellet, R is Resistance measured, l is thickness of the pellet.

### 3.2.6 Dielectric properties

Ferrite materials are very often good dielectrics. For most applications of ferrite materials, the dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan$\delta$) are important practical parameters, and studies of the dielectric properties provide a great deal of information about the suitability of the material for various applications.
Dielectric Constant ($\varepsilon'$)

For a given substance, the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric is called dielectric constant of the substance. It is a measure, therefore, of the amount of electrical charge a given substance can withstand at a given electric field strength.

The capacitance, $C$ for a parallel plate capacitor is given by

$$C = \varepsilon_o \frac{A}{t}$$  \hspace{1cm} (3.6)

where $\varepsilon_o$ is the permittivity of free space and is equal to $8.854 \times 10^{-12}$ F/m, $A$ is the area of electrode and $t$ is the separation between two electrodes.

When a dielectric (electrical insulator) fills the space between the plates, the capacitance of the capacitor is increased by a factor $\varepsilon'$, which is called the dielectric constant of the dielectric material. Therefore, for a parallel plate capacitor with a dielectric between the capacitor plates, the capacitance, $C$ is given by

$$C = \varepsilon' \varepsilon_o \frac{A}{t}$$  \hspace{1cm} (3.7)

Thus the energy stored in a capacitor of a given volume at a given voltage is increased by the factor of the dielectric constant when the dielectric material is present.

For an alternating electric field, the dielectric constant can be written as

$$\varepsilon_r = \varepsilon' - i\varepsilon''$$  \hspace{1cm} (3.8)
where \( \varepsilon' \) is the real component of the dielectric constant, in phase with the applied field. \( \varepsilon'' \) is the imaginary component, 90° out of phase with the applied field, caused by either resistive leakage or dielectric absorption. For normal substances, the value of \( \varepsilon_r \) is low, usually under 5 for organic materials and under 20 for most inorganic materials.

**Dielectric Loss tangent (\( \tan\delta \))**

The charging current in an ideal dielectric leads the applied voltage by \( \pi/2 \) radians (90°). However, in real dielectrics in addition to the charging current associated with the storage of electric charge by the dipoles, a loss current must also be considered. The loss current arises from the long-range migration of charges, e.g., dc ohmic conduction and the dissipation of energy associated with the rotation or oscillation of dipoles. As the dielectric is not loss free, it is generally represented by a complex dielectric constant, defined in equation 3.8. The total current in the real dielectric is a complex quantity which leads the voltage by an angle (90-\( \delta \)), where \( \delta \) is called the loss angle. Dielectric loss tangent (\( \tan\delta \)) also known as dissipation factor is defined as \( \tan\delta = \varepsilon''/ \varepsilon' \). The inverse of the loss tangent, \( Q = (1/\tan\delta) \), is used as a figure of merit in high frequency applications.
References


