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 $\text{H}_2\text{O}$ 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 ($\lambda$), the constructive interference occurs for a fixed set of an interplaner spacing ($d$) and incidence angle ($\theta$) (Figs. 3.3 & 3.3). According to Bragg’s condition of diffraction:

$$\lambda = 2dsin\theta$$ \hspace{1cm} 3.1

For cubic system, $d$ is given by

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$ \hspace{1cm} 3.2

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

$$\sin^2\theta = \frac{2}{4a^2}(h^2 + k^2 + l^2)$$ \hspace{1cm} 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](image)

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:

\[
B = \frac{k\lambda}{L \cos\theta}
\]

where \(B\) is the broadening of line expressed in the unit of \(2\theta\), \(K\) is a constant \(\approx 1\) in most case and \(L\) 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.

- **Target:** Cu-Kα
- **2θ range:** 20-80°
- **Step width:** 0.02,
- **Count rate:** 400-700 counts/sec.

### 3.2.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a well known technique for imaging solid materials at atomic resolution. Structural information can be acquired both by (high resolution) imaging as well as by electron diffraction. Additional detectors allow for elemental and chemical analysis down to this sub-nanometer scale.

**Basic principles**

The design of a transmission electron microscope (TEM) is analogous to that of an optical microscope. In a TEM high-energy (>100 kV) electrons are used instead of photons and electromagnetic lenses instead of glass lenses. The electron beam passes an electron-transparent sample and a magnified image is formed using a set of lenses. This image is projected onto a fluorescent screen or a CCD camera. Whereas the use of visible light limits the lateral resolution in an optical microscope to a few tenths of a micrometer, the much smaller wavelength of electrons allows for a resolution of 0.2 nm in a TEM.
**Imaging**

Image contrast is obtained by interaction of the electron beam with the sample. Several contrast effects play a role. In the resulting TEM image denser areas and areas containing heavier elements appear darker due to scattering of the electrons in the sample. In addition, scattering from crystal planes introduces diffraction contrast. This contrast depends on the orientation of a crystalline area in the sample with respect to the electron beam. As a result, in a TEM image of a sample consisting of randomly oriented crystals each crystal will have its own grey-level. In this way one can distinguish between different materials, as well as image individual crystals and crystal defects. Because of the high resolution of the TEM, atomic arrangements in crystalline structures can be imaged in large detail.

**Electron Diffraction**

By adjusting the magnetic lenses such that the back focal plane of the lens rather than the imaging plane is placed on the imaging apparatus a diffraction pattern can be generated. For thin crystalline samples, this produces an image that consists of a pattern of dots in the case of a single crystal, or a series of rings in the case of a polycrystalline or amorphous solid material. For the single crystal case the diffraction pattern is dependent upon the orientation of the specimen and the structure of the sample illuminated by the electron beam. This image provides the investigator with information about the space group symmetries in the crystal and the crystal’s orientation to the beam path. This is typically done
without utilising any information but the position at which the diffraction spots appear and the observed image symmetries.

Diffraction patterns can have a large dynamic range, and for crystalline samples, may have intensities greater than those recordable by CCD. As such, TEMs may still be equipped with film cartridges for the purpose of obtaining these images, as the film is a single use detector.

In case of a crystalline material, electron diffraction will only occur at specific angles, which are characteristic for the crystal structure present. As a result, a diffraction pattern of the irradiated area is created that can be projected onto the CCD camera. In this way, electron diffraction can provide crystallographic information from thin films, bulk materials as well as from nanometer sized particles (figure 3.4).

![Fig. 3.4 (a): Crystalline diffraction pattern from a twinned grain of FCC Austenitic steel](image1)

![Fig. 3.4 (b): Electron diffraction patterns of an as-deposited (room temperature) and an annealed (300 °C) Al-Ge film. The left part shows a set of a few, broad rings, characteristic of an amorphous film. The right part shows a large number of sharp rings. The diameters of these rings are characteristic for the crystal structure present. In this case a mixture of crystalline Al and crystalline Ge.](image2)
**Chemical analysis**

As a result of the interaction of the electron beam with the specimen, some energy is transferred from the electrons to the sample. The excitation and de-excitation of atoms and molecules in the sample allow (local) chemical analysis. This analysis can either be performed using the broad beam used for normal imaging, or by focusing the beam size down to 0.2 nm. The combination of Scanning TEM (STEM), a mode in which this narrow beam scans a selected area of the specimen, with chemical analysis techniques such as Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-Ray analysis (EDX) allows for mapping of the lateral distribution of elements with high spatial resolution.

### 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 Elmer 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 \([1]\). Using the analysis of Waldron \([2]\), the force constant \(K_0\) and \(K_t\) 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 \([3]\). 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 approached 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.

![Hysteresis Curve Diagram](image)

**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 (Ms), coercivity (Hc), remanence magnetization (Mr) 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,

\[ \rho = \frac{R \cdot A}{t} \]  

where, A is cross-sectional area of the pellet, R is Resistance measured, t 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

$$C = \varepsilon_0 \frac{A}{t} \quad 3.6$$

where $\varepsilon_0$ 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

$$C = \varepsilon' \varepsilon_0 \frac{A}{t} \quad 3.7$$
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

\[ \varepsilon_r = \varepsilon' - i\varepsilon'' \]

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 (tanδ)**

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 (tanδ) also known as dissipation factor is defined as \( \tan \delta = \varepsilon''/ \varepsilon' \). The inverse of the loss
tangent, \( Q = \frac{1}{\tan \delta} \), is used as a figure of merit in high frequency applications.

**References**

