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3.1 INTRODUCTION

Magnetic oxides which are commonly known as ferrite are the most important and rather the only relevant materials from the point of view of their application. They are being studied for last five to six decades for their basic properties such as structural, magnetic and electrical properties. Recently, focus is on the synthesis and characterization nano-crystalline ferrites which exhibit superior properties compared to their bulk counterpart.

Ferrites are ferrimagnetic semiconductors, opened a new area in the physics of material science and the need for high resistivity ferrites led to the synthesis of the various ferrites. The increasing demand for low loss ferrites resulted in detailed investigations on the various aspects of the conductivity and on the influence of the various substitutions on the electrical conductivity, thermoelectric power, hall mobility etc. The
electrical and magnetic properties of ferrites are depend upon the following factors

A) method of preparation [1],

B) site preference [2] and

C) valence distribution [3].

The present chapter has been devoted to describe the various experimental techniques used for the characterization of ferrites system studied in the present work. The polycrystalline ferrites with spinline structure prepared by ceramic method were studied using the following experimental techniques so as to determine their phase purity, unit cell parameter, infrared absorption modes, magnetic properties, Curie temperature and transport properties.

### 3.2 EXPERIMENTAL TECHNIQUES

The spinline ferrite system having the generic formula Co$_{0.7}$Zn$_{0.3}$Al$_{x}$Fe$_2$O$_4$ and Co$_{0.7}$Zn$_{0.3}$Cr$_x$Fe$_2$O$_4$ were prepared by standard double sintering ceramic method and were studied by X-ray diffraction, infrared spectroscopy, magnetization, a.c. susceptibility, d.c. electrical resistivity and dielectric properties.
3.3 METHODS OF SAMPLE PREPARATION

There are several methods of preparation of magnetic oxide systems with cubic structure (garnet) apart from standard ceramic method. These includes:

1. Wet chemical (co-precipitation) method [4-7].
2. Reactive hot pressing [8].
3. Simple self-propagating, gas producing, auto catalytic, novel combustion process [9,10].
5. Chemically synthesized precursors produced ferrite powders at low temperature [12].
6. Non-aqueous chemical route [13].
7. Preparation of Gallstones from processed stones [14].
8. Hot-spray reactor [15-17].
9. Ceramic method [18]. etc.

3.3.1 Ceramic method
The most common method of preparation of oxide garnet system is the ceramic method. The presently investigated systems have been synthesized by using the high temperature solid-state reaction method (ceramic method). In this technique, analar reagent (AR) grade oxides were weighed and mixed in stoichiometric proportions. The mixture was finely ground for few hours in an agate mortar using a liquid medium such as acetone. After grinding, 1 to 2 % of polyvinyl alcohol is added as a binder and then pressed into circular pellets of 10 mm diameter and 3 mm thickness under a pressure of 3 ton per square inch. The pellets are initially heated at 400 °C to remove the binder and then temperature of furnace was raised to 1000 to 1050°C (Presintering temperature) for 24 hrs. and then slowly cooled to room temperature.

After presintering process, the pellets were again finely ground, sieved through a 100 A0 mesh and pellets were made. In the final sintering process, the pellets were held at 1300 to 1350 °C for 24 hrs, and the samples were slowly cooled to room temperature, at the rate of 2°C per min. (All the heating and sintering stages were carried out using a programmable furnace).
Fig. 3.1 gives the flow chart of the various steps involved in the present method adopted for the sample preparation.

3.4 X-RAY DIFFRACTION

In order to establish definitely that X-rays have the same electromagnetic wave nature as ordinary light, it is necessary to demonstrate that X-rays can be reflected, refracted, diffracted, polarized and scattered like ordinary light. Experimental demonstration of these wave characteristics of X-rays started with positive results obtained by Prof. Laue and his co-workers in their attempts to produce diffraction of X-rays with crystals. These were followed up by the other experiments, which convincingly proved that X-rays could be reflected, refracted, polarized and scattered. We shall summaries here these experiments that bring out clearly the wave nature of X-rays.

**Experimental procedure**
Starting with a small glancing angle $\theta$ for the incident beam, which can be obtained by rotating the crystal table $T$, the beam is reflected from the crystal face and enters the ionization chamber set at an angle $2\theta$ to the incident direction. The rate of deflection of the needle of the electrometer is then a measure of the intensity of the reflected beam. The glancing angle is next increased, step-by-step, and the observations repeated, taking care to rotate the ionization chamber through twice to the angle through which the crystal table is turned. The intensity of ionization is plotted against the different values of the glancing angle. The curve obtained is shown in Fig. 3.2 is called as X-ray spectrum.

![Fig. 3.2 X-ray spectrum](image)
It is seen that only for certain values of $\theta$ the intensity of the reflected beam swells out as indicated by the sharp maxima. In the whereabouts of a given angle, say $\theta_1$, $\theta_2$ or $\theta_3$, there are more than one maximum two $A_1B_1$, $A_2B_2$, $A_3B_3$, in the figure. These maxima are due to X-rays of two different wavelengths contained in the incident heterogeneous beam from the X-ray tube.

Taking only the prominent peaks $A_1$, $A_2$, $A_3$, the glancing angles corresponding to them, $\theta_1$, $\theta_2$, $\theta_3$, can be obtained from the graph. It is found that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 : : 1 : 2 : 3$ nearly, which shows that the peaks $A_1$, $A_2$, $A_3$, refer to the first, second and third order reflections respectively. In a similar manner, measuring the angles corresponding to the smaller peaks $B_1$, $B_2$, $B_3$ the same proportionality between the signs of these angles is found. Using Bragg’s relation it can be shown that $A_1$, $A_2$, and $A_3$ refer to X-rays of the same wavelength; likewise $B_1$, $B_2$, and $B_3$. Evidently $A_1$, $B_1$ belongs to the first order spectrum, $A_2$, $B_2$, to the second order and so on [19].

X-ray diffraction technique is a useful tool for the study of crystal structure of materials [20, 21]. The technique is also
useful for the determination of crystal structure, chemical analysis, phase equilibria, a particle size etc. The XRD patterns for all the samples were recorded at TIFR Mumbai, on a Phillips make X-ray diffractometer (Model PW 3710). X-ray diffractometer technique is used to confirm the single-phase nature of the samples, to determine the structural parameters such as lattice constant, X-ray density, particle size etc. The following specification has been employed for XRD patterns.

- Target used Cu Kα
- Scanning rate 2°C per minute
- Range of 2θ is 20° to 80°

In the method of X-ray diffraction the powder material is placed in a beam of monochromatic X-rays, each particle of the powder tiny crystallite oriented at random with respect to the incident beam. In crystals, atoms are arranged in a pattern periodic in three dimensions. It may be possible that some of the particles are correctly oriented for say (100) planes and can reflected the incident beam while other particles can reflect for (hkl). As X-ray has electric field associated with it, this field interacts with electron clouds of atoms, due to its short
wavelength it is scattered by adjacent atoms in crystals. If the interference between these scattered rays is constructive, diffraction phenomenon is observed. The condition for constructive interference in terms of inter planer spacing \( d \) and the glancing angle \( \theta \) is,

\[ n\lambda = 2d \sin \theta. \tag{3.4} \]

where, \( \lambda \) is wavelength of X-ray radiation, \( d \) is inter planer spacing and \( \theta \) is the glancing angle measured from the position of Bragg’s peak.

For the ferrite (garnet) having cubic structure the inter planer spacing \( d_{hkl} \) is obtained using the following relation

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{3.5} \]

or

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.6} \]

where, \( a \) is lattice constant, \((hkl)\) is Miller indices. Using equation (3.5)

\[ \sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2(h^2 + k^2 + l^2)} \tag{3.7} \]

where,
\( \lambda \) is incident wavelength.

In equation (3.7) the sum \( (h^2+k^2+l^2) \) is always an integer, while \( \lambda^2/4a^2 \) is constant for any one pattern. The indices of different planes of a diffractogram for the cubic system can be written as

\[
\frac{\sin^2 \theta_{hkl}}{(h^2+k^2+l^2)} = \frac{\lambda^2}{4a^2} \tag{3.8}
\]

The lattice parameter ‘a’ can be determined using the formula

\[
a = d N^{1/2} \tag{3.9}
\]

where,

\[ N = (h^2+k^2+l^2) \]

The X-ray density \( (d_x) \) can be computed using the following relation

\[
d_x = \frac{8M}{Na^3} \tag{3.10}
\]

where,

\[ M \text{ is Molecular weight of sample and } N \text{ is Avogadro’s number (6.023 x 10}^{23}) \].
3.5 **SCANNING ELECTRON MICROSCOPY**

The scanning electron microscopy is one of the powerful techniques used to analyze the microstructure of the ferrites. The scanning electron microscopy (SEM) was first developed by Von Avdenne [22] and is used for determination of the grain size, porosity, grain boundary. The relation between microstructure and porosity assumes a variety of forms in ferrites.

3.6 **INFRARED SPECTROSCOPY**

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 200 cm$^{-1}$-1000 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 [23]. Using the analysis of Waldron [24], the force constant $K_0$ and $K_t$ were calculated.

3.7 MAGNETIZATION

The saturation magnetization, coercivity, remanance magnetization etc. magnetic properties were measured using
pulse field magnetic hysteresis loop tracer supplied by Magneta company (Mumbai). The measurements were carried out at room temperature. The system consists of pulse power supply, solenoid and pick up coil assembly, signal processor and data acquisition system.

1. **Solenoid and Pick-up Coil Assembly:**

   The solenoid is wound on a high quality Bakelite former with an enameled copper wire. A pickup coil system is wound with a fine copper wire on a former concentric with the solenoid. It consists of 2 main windings whose resultant voltage is very nearly balanced. An additional winding is used for perfect balance. The output of this winding is connected to a balancing network consisting of a magnitude and phase balance. The assembly containing the solenoid and pickup coil is housed in an acrylic box.

2. **Signal Processor:**

   The signals produced in the pickup coil are proportional to the rate of change of magnetization of the sample as well as to the applied field. These are processed using integrating, amplifying
and phase correcting circuits to produce signals representatives of magnetization of the sample and the applied magnetic field.

3. **Data Acquisition System (DAQ):**

The Data Acquisition System consists of a micro-controller with fast digitizing and high resolution circuit. The digitized data is sent to PC through a RS-232 port. Special software is designed to plot the hysteresis loop and display the hysteresis parameters.

Measurement was taken after applying magnetic field of 5 KOe having the magnetization sensitivity 10 emu with accuracy 1 to 5 %. High magnetic field is generated in a solenoid by passing a pulse current of sinusoidal shape. A pickup coil system is kept in the solenoid to detect field and magnetization signal of a sample placed in the pickup coil. The signals produced are then processed by an electronic system. These transitory signals are digitized by a micro-controller and then sent to computer for plotting a hysteresis loop, which is observed on the monitor with calculated values of hysteresis parameters. The experimental setup is shown
in Fig. 3.2. The block diagram of the instrument is depicted in Fig. 3.3. A typical hysteresis loop is shown in previous chapter (Fig. 2.5). The hysteresis loop gives the values of coercivity (Hc), remanent magnetization (Mr) and saturation magnetization (Ms).

3.8 A.C. SUSCEPTIBILITY MEASUREMENTS

The experimental setup for the thermal variation of a.c. susceptibility is as shown in Fig. 3.4. The Curie temperature of each sample was determined from the low field a.c. susceptibility data.

The measurements of a.c. susceptibility were carried out in the temperature range 300–800 K. From the plots of $\chi_T/\chi_R$ versus temperature, Curie temperature of the sample is obtained.

The Curie temperature setup comprises of

1) A.C. susceptibility unit,
2) Solenoid and pickup coil assembly,
3) Platinum furnace,
4) Furnace power supply,
5) Thermocouple and temperature indicator.
1. **A.C. susceptibility unit: Model ACS 2A**

   The schematic diagram of the a.c. susceptibility unit is given in Fig. 3.5. It consists of function generator, balancing circuit and signal processing circuit based on lock-in amplifier principle.

2. **Solenoid and pickup-coil assembly**

   The pickup coil is wound in two sections comprising three windings. The main two windings are identical and wound in opposition direction. The sample under test is placed in the vicinity of one of the windings producing a differential voltage proportional to the magnetization of the sample.

3. **Platinum furnace**

   The sketch of the furnace is shown in Fig. 3.6. The platinum wire is wound on a quartz tube of diameter 18 mm and wrapped with a fiber glass ribbon and pushed tightly in another quartz tube. The furnace is introduced in a double wall jacket which can take water for cooling the outer region of the furnace. This whole
assembly is put into the solenoid and then held in plastic container.

4. **Furnace power supply**

   It is a regulated d.c. power supply whose voltage and current can be varied continuously in the range 0-30 volts, 0-5 amperes respectively.

5. **Thermocouple and temperature indicator**

   The thermocouple used to measure the temperature of the furnace was platinum-platinum-rhodium (13%) junction, which is terminated into a linear temperature indicator and also into one channel of Data Acquisition System (DAS). When the thermocouple is in good contact with the samples, the temperature indicator directly reads the temperature of the sample.

   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,

\[ \rho = \frac{R \cdot A}{t} \]  \hspace{1cm} (3.11)

where,

A is cross-sectional area of the pellet

R is Resistance measured

t is Thickness of the pellet
The temperature dependence of d.c. resistivity for all the samples.

3.9 DIELECTRIC PROPERTIES

Electrical conductivity and dielectric behaviour in ferrites depends on many factors such as preparation method, sintering temperature, amount and type of substitution. They exhibit relatively high resistivity at carrier frequency, sufficiently low losses for microwave applications and wide range of other electrical properties.

The dielectric measurements were made using the two-probe method. Air-dried silver epoxy paste was applied on the flat surface of the sintered pellets. The a.c. parameter such a dielectric constant ($\varepsilon'$) dielectric loss ($\varepsilon''$) and loss tangent (tan\(\delta\)) depend on the frequency under investigations. The measurements of a.c. resistance (R) and capacitance (C) were measured with the help of LCR-Q meter (HP 4284A) in the frequency range 100Hz - 5MHz. The variation of dielectric
properties with temperature was also studied. Assuming the capacitance of parallel plate arrangement the dielectric constant ($\varepsilon'$) is calculated using the following relation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (3.12)$$

where, \(C\) is capacitance, \(d\) is thickness of pellet, \(\varepsilon_0\) is permittivity of the free space, \(A\) is cross sectional area of pellet.

The dielectric loss ($\varepsilon''$) was calculated using the relation

$$\varepsilon'' = \frac{\sigma}{2\pi \cdot \varepsilon_0 f} \quad (3.13)$$

where, \(\sigma\) is a.c. conductivity,

The dielectric loss tangent (\(\tan\delta\)) was calculated using the relation

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (3.14)$$

The frequency dependence of dielectric constant ($\varepsilon'$) dielectric loss ($\varepsilon''$) and loss tangent ($\tan\delta$) of all the samples were carried out at room temperature.

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Fig. 3.1. Flow chart of stages involved in preparation of spinel ferrite by ceramic method.
**Fig. 3.2** Experimental setup for Hysteresis loop technique
Fig. 3.3  Schematic of pulse field hysteresis loop tracer system
Fig. 3.4 Experimental setup for thermal variation of a.c. susceptibility.
Fig. 3.5 Schematic block diagram of a.c. susceptibility system
**Fig. 3.6** Platinum Furnace assembly