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## **Chapter 3. Experimental techniques**

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### **3.1 Introduction**

Ferrites launched a new branch in the material science. Ferrites are the ferrimagnetic oxide which is semiconductor in nature. The synthesis of the different ferrites with high resistivity due to the large demand in modern technology in recent years. This growing interest demand for low loss ferrites led to investigate in detail on the different features of the conductivity and the effect of the several doping elements on the electrical conductivity, magnetic property and hall mobility etc. The magnetic and electrical properties of ferrites depends on many factors e.g, method of preparation, synthesis parameters, site preference and cation distribution etc. [145-147].

Different experimental techniques have been employed in the present investigations for the studies of the ferrites have been described in this chapter. Description of preparation of materials along with their characterization is presented. The experimental methods have been taken and the description of different instruments employed to study the XRD pattern, structural morphology and microstructure, magnetic properties, conductivity, dielectric and electrical properties are presented.

## **3.2 Sample synthesis**

Material preparation is the most crucial part of synthesizing new materials with differing properties. There are numerous techniques accessible for the preparation of different materials. Here some of the synthesis techniques are shortly summarised.

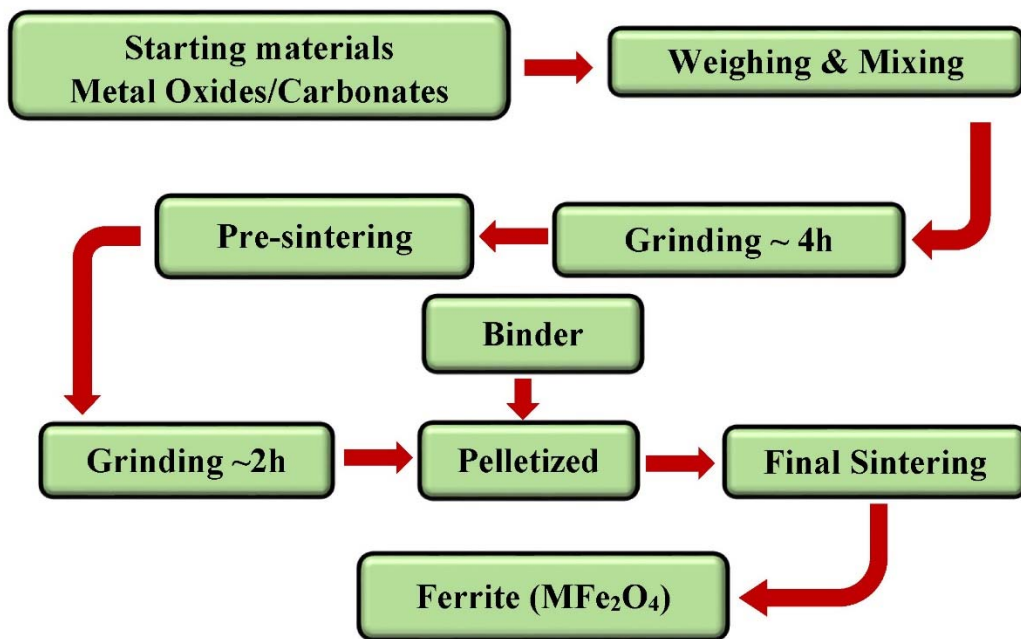
### ***3.2.1 Solid state reaction method***

The commonly utilized method for the fabrication of bulk ferrites is the solid-state reaction method or ceramic method [116, 177-179]. This method is straightforward and more advantageous than other methods e.g. sol-gel, co-precipitation etc. [118, 180]. It does not require much chemical knowledge to adopt. The significant disadvantage of this method is that the final sample has some extra phases. Vital steps in this method are calcinations and sintering. Temperature and time of calcination and sintering varies from system to system.

In the ceramic method, ferrites are commonly produced from the powders of Iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ) and metal (II) oxides such as  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$  and  $\text{MoO}_3$  etc. by a chemical reaction referred as calcinations. Then the mixture is crushed to particles smaller than  $2\ \mu\text{m}$  to create Weiss domains of the size of a single particle. Afterwards, the powder is palletized by mixing polyvinyl binder, dried and then sintered.

Grinding and mixing of the oxide mixtures have more significance for the homogeneity of the predicted phase. In sintering, the pellets of the sample must be heated at high temperature without melted. Anyway, solid state reaction method is very slow. It is

executed at very high temperatures ( $>1100^{\circ}\text{C}$ ), where responding particles can diffuse through solid materials to occur the reaction easily. The ferrites synthesize through ceramic route are in bulk form. The size of the particles is in micrometer range ( $10^{-6}\text{m}$ ). All the steps in the ceramic route to prepare ferrites are schematically displayed in the flow chart below (Fig 3.1).



**Fig. 3.1.** Schematic representation of different steps involve in solid state reaction method.

Commonly, spinel ferrites are prepared with the help of the following steps in the solid state reaction technique.

*(a) Starting compounds*

At the first step, powder of ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and other metal oxides are taken for synthesizing the expected ferrite compounds. Metal carbonates may also be utilized.

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Carbon dioxide will be removed as the gaseous form at the time of sintering and hence, the metal carbonates are changed into metal oxide.

### *(b) Weighing*

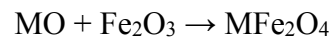
All the raw materials are carefully weighed with the proper stoichiometric ratio to get the ferrite material with predefined molecular concentration.

### *(c) Grinding*

Good mixing and small particle size can be accomplished by grinding of the powder mixture in addition of volatile acetone by using the agate mortar and pestle. This diminishes the porosity of the desired sample. The acetone will be separated by firing and the fine ferrite powder will be found. Mixing and grinding should also be possible in an electric grinder or in ball milling.

### *(d) Pre-sintering*

Pre-sintering will be done in the presence of air and the temperature is about 1200°C for about 36 hours. In this step, the ferrite will partially form:



This stage creates a uniform last material and decreases the shrinkage which will happen in final sintering.

### *(e) Grinding*

In this step, the powder is again ground to induce the mixing of un-reacted oxides and to decrease the particle size.

#### *(f) Pelletize*

At that stage, dry powder of the sample is mixed with the water soluble organic binder like PVA. The final shape of the powder has been achieved by applying the uniaxial pressure of 10 to 20 tons/in<sup>2</sup> by a hydraulic press. Cylindrical and toroidal are most common shapes.

#### *(g) Sintering*

It is the final and crucial stage in the fabrication of ferrite by the ceramic method. The heating and cooling cycle extends about 12-24 hours. The temperature at the time of sintering changes from 1100<sup>0</sup>C to 1400<sup>0</sup>C. During sintering, there is interdiffusion between neighboring particles takes place and stick together. By the diffusion of vacancies to the surface, the porosity is decreased. Strict control of temperature and atmosphere of the furnace is vital as these variables have marked impacts on the magnetic behaviors of the product sample.

### **3.3 Crystal structure: X-ray diffraction**

X-ray diffraction (XRD) is treated as the most accomplished non-destructive analytical technique for the analysis of multiphase mixture both qualitatively and quantitatively. It is also used to identify the amorphous or polycrystalline nature of samples. Many substances can have the crystal form such as semiconductors, metals, salts, minerals, as well as different organic, inorganic, biomolecules etc. in the advancement of various scientific discipline, X-ray crystallography has a significant role to play. In the first decade of X-ray crystallography, it is used figure out the atomic size, the characteristics of chemical bonds

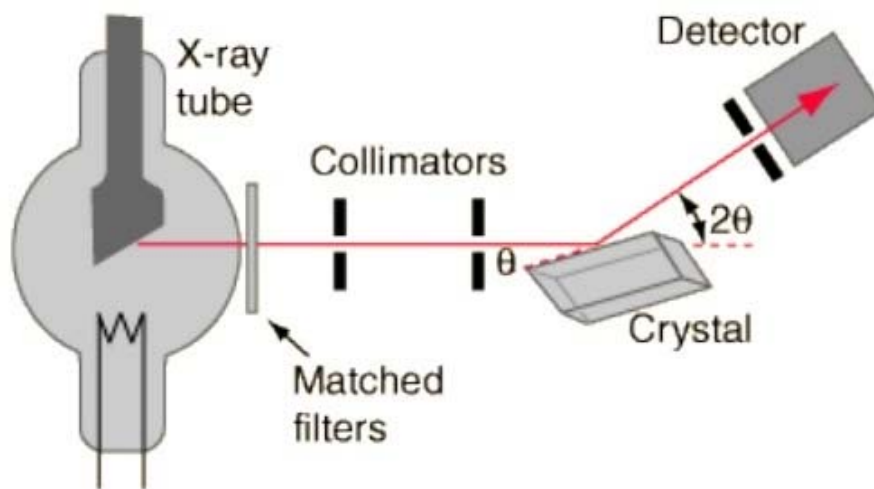
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and the atomic-scale differences of several materials like minerals and alloys. This technique also displays the structure and functions of various biomolecules e.g., protein, vitamins, drugs, and DNA etc. X-ray crystallography is, however, the primary approach for describing the atomic structure of the synthesized new substance. This method can also identify the strange electronic or elastic behavior of a material, shed light upon the chemical interactions and serve as the principle for developing pharmaceuticals.

The X-ray diffraction pattern provides the information regarding the phase purity of crystalline samples, crystallite sizes, solid solution, stress and texture, density etc. However, XRD patterns offer the knowledge of the Bragg's peaks positions [181]. The XRD pattern allows to detect the presence of structural phases in the final product accomplished by the technique of synthesis deployed. The single phase nature, particle size, unit cell parameter, cation distribution, X-ray density etc. structural parameters can be acquired from analysis of XRD data. In addition to this, XRD pattern provides better conclusive structural information, interatomic distance and bond angles etc. X-ray diffraction pattern also furnished the information about the structure to probe atomic distances which need a probe wavelength of the order of 1 Å [182]. The schematic diagram of Bragg's X-ray spectrometer is presented in Fig. 3.2.

To measure the X-ray diffraction data, the sample is mounted on a goniometer which is smoothly rotated in front of incident X-rays. This yield a diffraction pattern which contains alternative dark and bright spots termed as reflections. The two-dimensional XRD patterns are transformed into a three-dimensional model of electrons density of the crystal by utilizing the Fourier transforms, linked with the chemical information of the sample.

The resolution becomes poor if the crystallite size of the samples is very small or not uniform.



**Fig. 3.2.** The schematic diagram of Bragg's X-ray spectrometer.

An X-ray diffractometer irradiates the sample with known wavelength X-rays. The sample and detector are moved accordingly to measure the intensity of reflections with the angle of diffraction. From the intensity vs. angle ( $2\theta$ ) plot one can conclude the structure of the material.

The extensively utilized X-ray diffraction technique for describing the structure of materials is the powder method in which the sample is usually in a powder form. When the X-ray monochromatic beam of falls on powder specimen, it's reflected and the reflected beams interfere. If the path difference between the interfering rays is equal to the integral multiple of the wavelength of the incident X-ray Then the interference is constructive only.

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Depending on the nature and size of the unit cell, the atomic number and position of the different atoms in the structure, different crystalline materials produce their own distinct diffraction patterns. The lattice planes are oriented in all possible directions, in which some are oriented in Bragg angle  $\theta$ , to the incident beam, satisfying the Bragg's law. Bragg's law gives condition of constructive interference as [183]

$$2d(\sin\theta) = n\lambda \quad (3.1)$$

where,  $d$  and  $\lambda$  are the inter-planer spacing and the X-ray wavelength respectively and  $n$  is the order of diffraction. Here we are using the Philips PANalytical X-ray diffractometer (Fig. 3.3) in which Cu (Copper) is used as the target. The wavelength of the  $K\alpha$  radiation is  $\sim 1.5402\text{\AA}$ .



**Fig. 3.3.** The PANalytical X-ray diffractometer (Central Research Facility, IIT Kgaragpur, West Bengal).



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Few other methods which incorporate X-ray to figure out the atomic structures. Similarly, the scattering of electrons or neutrons is used to produce diffraction patterns, which are interpreted by using Fourier transform. Also, some other methods like fiber diffraction and small-angle X-ray scattering (SAXS) are used to characterize the crystalline samples. Electron diffraction technique is employed if the sample has poor crystallinity or in the form of nano-crystalline powders

In all the X-ray diffraction methods mentioned above, the scattering is elastic, i.e. the wavelength of the incident and scattered X-rays are same. Also, the inelastic X-ray scattering is used to study the atomic excitations rather than its distribution in the sample.

### **3.4 Dielectric and electrical measurement**

Impedance analyzer or an LCR meter (Inductance (L), Capacitance (C), and Resistance (R)) gives extremely exact and intensive component for material assessment with different test conditions. It measures impedance (inductance, capacitance, and resistance) at a particular temperature/frequency or across a range of temperatures/frequencies. Advanced model of Impedance analyzer can measure the true inductance or capacitance. It also measures the equivalent series resistance and the Q factor of the active components. The Impedance Analyzer is interfaced to the computer and the data (capacitance, dielectric loss, inductance and AC conductivity) is collected as a function of frequencies.

Usually, the sample is subjected to an AC power source [184]. The analyzer measures the potential drop and the current through the sample. The analyzer estimates the magnitude of the impedance from the ratio of these potential and current. The phase

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difference between the voltage and current along with the impedance, capacitance, inductance, and resistance of the sample can also be calculated and displayed. The analyzer assumes a parallel model for the CR measurements and a series model for the LR measurement. So the equivalent electrical circuit of a ceramic sample can be characterized by a parallel combination of capacitance ( $C_p$ ), and a frequency dependent resistance due to short range polarization  $R_{ac}(\omega)$  and a dc resistance  $R_{dc}$  because of a long-range movement of charge carriers.  $C_p$  and  $R_p$  (the parallel combination of  $R_{ac}$  and  $R_{dc}$ ) are the equivalent capacitance and resistance measured by the analyzer for estimating the dielectric constant and the loss tangent.



**Fig. 3.4.** LCR meter and impedance analyzer (Newton4th Ltd. PSM1735) (Magnetism and Magnetic Material Laboratory, IIT Kharagpur, West Bengal).

It may be noted that the resistance  $R_p$  in parallel arises due to a combination of both ac and dc conductivity [ $\sigma_{ac} + \sigma_{dc}$ ] in the sample. Dielectric loss tangent of a dielectric material at a given frequency  $\omega$ , is given by,

$$\tan\delta = \frac{1}{\omega R_p C_p} \quad (3.2)$$

And the dielectric constant ( $\epsilon$ ) can be calculated from the capacitance utilizing the equation,

$$\epsilon = \frac{Cd}{\epsilon_0 A} \quad (3.3)$$

where, C is the capacitance of the sample in Farad (F), d is the distance between the two electrodes in meters (m), A is the area of the pellet in square meters (m<sup>2</sup>) and  $\epsilon_0$  is the free space permittivity.

Newton4th Ltd. PSM1735 Impedance Analyzer (Fig. 3.4) was deployed to measure the real and imaginary part of impedance ( $Z'$  and  $Z''$ ), dielectric constant, dielectric loss, electric modulus and AC conductivity etc. of all the samples. To do the temperature dependent study the samples were placed in an oven in which temperature up to 550<sup>0</sup>C can be achieved.

### **3.5 Magnetic measurement**

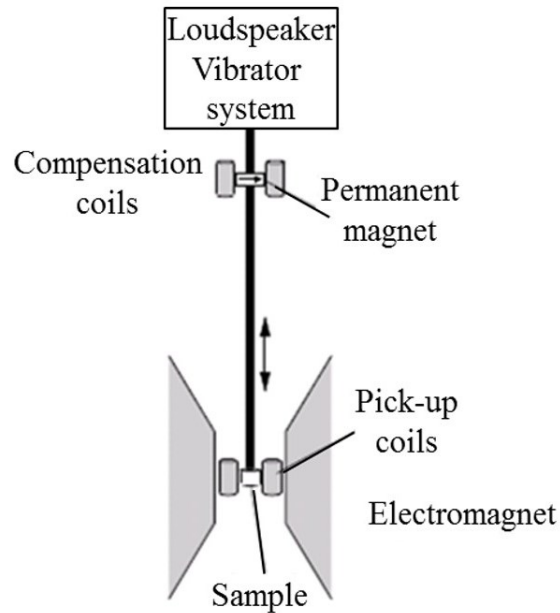
All of the magnetic properties measurements were accomplished by a commercial vibrating sample magnetometer (VSM) [185, 186] and a Quantum Design superconducting quantum interference device (SQUID) magnetometer [187].

#### **3.5.1 Vibrating sample magnetometer (VSM)**

Vibrating sample magnetometer is a useful device for the measurements of hysteresis loop and magnetic properties (saturation magnetization, residual magnetization etc.) of nano and bulk magnetic materials. Vibrating sample magnetometer or VSM was invented

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at Lincoln Laboratory MIT by Simon Foner in 1955 [188]. The paper about his work was published shortly in late 1959 [189]. The thought was also published by G. W. Van Oosterhout [190] and by P. J. Flanders [191].



**Fig. 3.5.** Schematic diagram of Vibrating Sample Magnetometer (VSM).

The schematic diagram of Vibrating Sample Magnetometer is depicted in Fig. 3.5. The principle of working of VSM is according to Faraday's law. Whenever magnetic flux linked with a conductor changes, an e.m.f will be induced in the conductor. In VSM, the specimen is magnetized by a homogeneous magnetic field and it is vibrated sinusoidally at small constant amplitude with respect to stationary pick up. A dipole moment will be produced in the magnetic specimen when it is exposed to a homogeneous magnetic field. This induced dipole moment is proportional to the product of material susceptibility and

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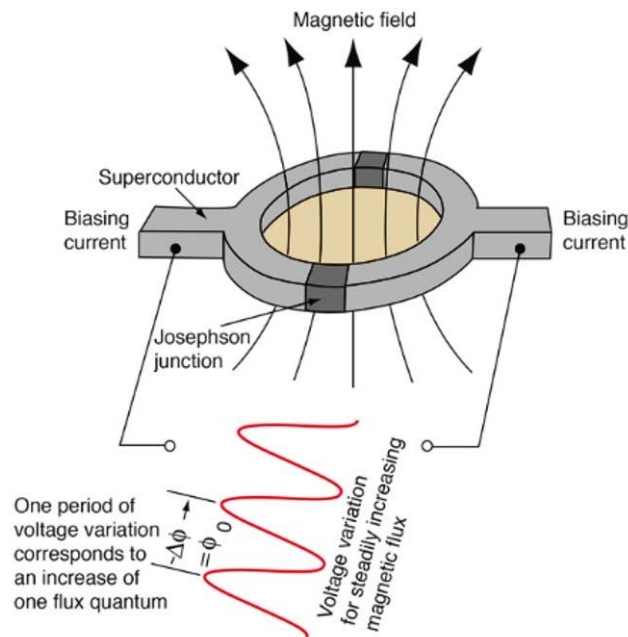
the external magnetic field. The system used a transducer assembly to vibrate the magnetic sample in a direction perpendicular to the applied magnetic field and a particularly located pick-up coils can produce an electric signal around the sample [189]. This induced e.m.f at the vibrating frequency is proportional to the induced magnetic moment in the material and both the amplitude and frequency of vibration. Therefore, to get the magnetic moment of the sample, a comparison voltage is induced in the same set of reference coils by a vibrating capacitor, which is vibrated by the same transducer. This comparison signal changes with the amplitude of vibration and the vibration frequency in the similar way as does the signal from the pickup coils placed near the sample. These two signals are applied to two inputs of a differential amplifier to cancel the effects of amplitude and the frequency of vibration. Therefore, the signal at the output of the differential amplifier is now only a function of the magnetic moment of the specimen. The output signal of the differential amplifier is then applied to a synchronous detector (lock-in amplifier) where it is compared with a reference signal at its internal oscillator frequency and is also applied to the transducer, which oscillates the sample. Therefore the output is a signal proportional to the amplitude of the magnetic moment. This output signal is then amplified and used in two different ways. First part is feedback to the movable plate assembly of the vibrating capacitor and second part is moved to the output display circuits, where the amplitude of the moment is recorded. The effect of the feedback is to adjust the signal to the level required to maintain the capacitor output signal at the same level as the pickup coil signal. It is a very sensitive device and can detect a very small change in the value magnetic moment.

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For the measurements using VSM, the powered ferrite sample was weighted and pressed into a small quartz container and then mounted at the end of a rigid ceramic rod. In order to avoid the movement of the powers inside the tube, they were compacted using Teflon tape.

### 3.5.2 Superconducting quantum interference device (SQUID)

SQUID magnetometers have a higher sensitivity than VSM. Here the resolution obtained in a SQUID magnetometer is of the order of  $10^{-8}$  emu. SQUID magnetometer is used for measuring those samples which have a lower magnetic moment. The working principle of this device is mainly on the basis of the tunneling of superconducting electrons (the Cooper pairs) through an extremely thin insulating gap between two superconductors, known as Josephson junction, [192].



**Fig. 3.6.** Schematic diagram of Superconducting Quantum Interference Device (SQUID) magnetometer.

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The SQUID magnetometer typically consists of the following components: A superconducting measuring current flows across the ring such that total super-current is divided into two part and pass through the two identical Josephson junctions (A and B). When a magnetic field is applied, a magnetic flux  $\Phi$  goes through the superconducting loop and induces a persistent current  $J$ , based on Faraday's Law. The induced current adds to the measuring current in one junction ( $I_A$ ), and subtracts in the other ( $I_B$ ). When the current waves flow through the junctions their phase shifted by  $\delta_A$  and  $\delta_B$  respectively. Schematic representation of Superconducting Quantum Interference Device magnetometer in shown in Fig. 3.6.

Magnetic flux going through a superconducting loop is quantized. Hence there is interference between the currents after passing the junctions. When a material with magnetic moment is kept in the loop containing a Josephson junction, an e.m.f is induced in the loop, which induces a current with a frequency estimated by the Josephson equations. The SQUID detects the change in currents or frequency to reduce the magnetic moment of the sample.

#### ***3.5.3 Field cooled (FC) and zero field cooled (ZFC) measurement***

Zero Field Cooled (ZFC) data determines the type of different magnetic interactions ion different magnetic materials. To start with, the specimen is cooled in liquid helium temperatures without magnetic fields. Then a small homogeneous magnetic field is imposed and the magnetization is recorded while the specimen is heated at a steady rate. For tiny magnetic specimens, this plot has a characteristics shape. As the specimen cools

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in absence of an external magnetic field, they will have a tendency to magnetize along the favored crystal directions in the lattice to minimize the magneto-crystalline energy. As the arrangement of crystallites is arbitrary, hence, the resultant moment of the systems should be zero. Also when a little magnetic field is applied, the moments will stay locked into the favored directions, as found in the low-temperature region of the ZFC curve. When the temperature builds up, the thermal energy is high enough to disorient the system. Consequently much moments will orient themselves along the applied magnetic field to limit the Zeeman energy. Therefore, the required activation energy for the Zeeman interaction is delivered by the thermal vibration. As a result, the resultant moment of the system become greatest where the maximum population of moments has oriented along the applied field. The critical temperature is known as blocking temperature ( $T_B$ ) which relies upon the particle volume. As the temperature increases above  $T_B$ , thermal vibrations become sufficient enough to defeat the Zeeman interaction and hence randomize the magnetic moments [193].

Field cooled assessments is analogous to ZFC measurement apart from that the constant magnetic field is imposed when the sample is gone through both heating and cooling process. The resultant moment is normally recorded when the sample is heating. After all, the FC curve will deviate from the ZFC curve about the blocking temperature. The difference of the curve happens because every spin have a tendency to orient along the easy direction of the crystal which is nearest to the direction of the field applied and stay frozen in that alignment at lower temperature. Thermal Remnant Magnetization (TRM) curves can be achieved by cooling field to the initial temperature. After that the field is withdrawn



and the magnetization is estimated with variable temperature when the sample is heated again. It is to be noted that ZFC, FC, and TRM are non-equilibrium estimations [194, 195]. Special care should be taken to make sure that the similar rate of heating is employed at the time of the measurements to compare the data accurately.

### 3.5.4 Initial permeability

The initial permeability has been calculated by recording the inductance of solenoid with and without the ferrite core by the following method. The solenoid having diameter 5 mm and length 50 mm used for this purpose. This magnetic measurement has been performed by using a LCR meter (HIOKI 3532-50 LCR HiTESTER, Japan) as shown in Fig. 3.7.



**Fig. 3.7.** LCR meter (HIOKI 3532-50 LCR HiTESTER, Japan) (Magnetism and Magnetic Material Laboratory, IIT Kgaragpur, West Bengal).

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To measure the initial permeability of the sample a solenoid has 50 turns of SWG enameled copper wire is taken. The initial permeability was estimated by the equation given below as:

$$\mu_i = \frac{L}{L_0} \quad (3.4)$$

where,  $L = \frac{\mu_0 Ni}{l}$  and  $L = \frac{\mu_0 \mu_i Ni}{l}$ . Where,  $\mu_0$  is the free space permeability,  $N$  is number of turns,  $i$  is the current,  $l$  is the length of solenoid and  $\mu_i$  is the initial permeability.