# Chapter-3
Instrumentation

3.1 X – Ray Diffraction

X-rays are electromagnetic radiation of wavelength about 1 Å (10^{-10} m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma rays and the ultraviolet rays. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern, which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid-state chemistry and material science.

In our present work we have used Inel X-ray diffractometer with Co -Kα radiation with wavelength λ = 1.78897 Angstroms. These X-rays are allowed to fall onto the sample and the intensity of the reflected X-rays are recorded as a function of 2θ (Figure 3.1)
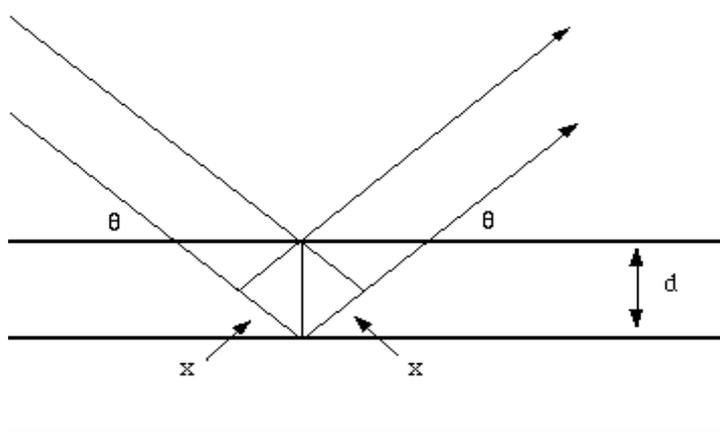
Figure 3.1: Reflection of x-rays from two planes of atoms in a solid

The path difference between two waves:

$$2\ x\ \lambda = 2\,d\,sin\theta \tag{3.1}$$

For constructive interference between these waves, the path difference must be an integral number of wavelengths:

$$n\ x\lambda = 2\,x \tag{3.2}$$

This leads to the Bragg equation:

$$n\,\lambda = 2\,d\,sin\theta \tag{3.3}$$

3.1.1 Instrumentation

The X-ray diffraction experiment requires an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays. Figure 3.2 is a schematic diagram of a powder X-ray diffractometer.
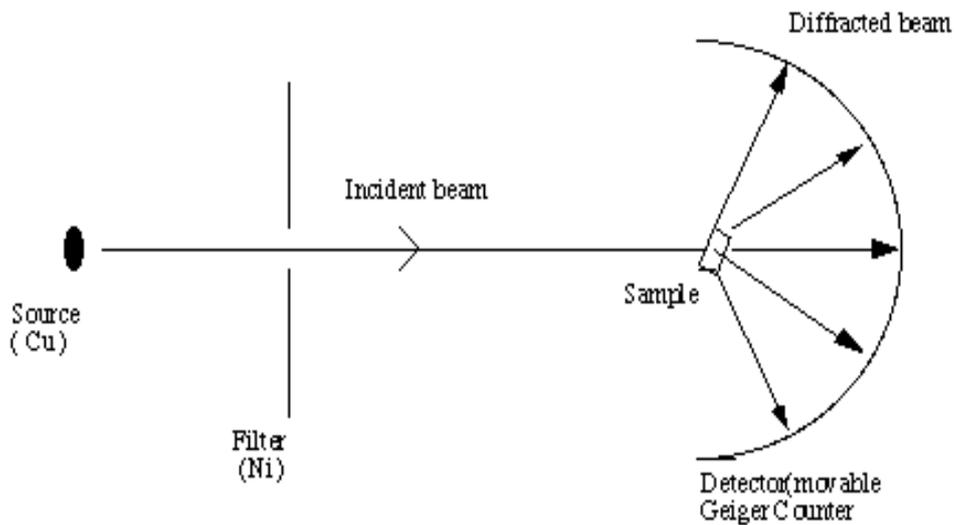

Figure 3.2: Schematic of an X-ray powder diffractometer

The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation is =1.5418Å. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2theta. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2theta values at a constant angular velocity. Generally, a 2theta range of 5^0 to 70^0 degrees is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2theta of 2degrees min^{-1} and therefore, about 30 minutes are needed to obtain a trace.

X-rays can be diffracted from crystals since their electric fields interact with the electron clouds of atom in crystals. The X-rays scattered from the adjacent atoms interfere and a diffraction pattern is produced. Bragg's law (equation 3.3) gives the condition for diffraction to occur from electrons in stacks of layers with an interplanar spacing'd'. The geometry of the diffraction pattern is determined by the size and shape of unit cell. While the intensities to the individual reflections from the accessible planes are controlled by the distribution of electron density within the cell.

Polycrystalline materials produce powder patterns in which the X-rays are diffracted not by one single crystal but by a sample consisting of a very large number of randomly oriented crystalline particles (a powder). When Bragg's law is satisfied for any given plane hkl all the reflections for all the tiny crystals lie on a cone with angle $2\theta_{hkl}$. The spots of the diffraction patterns of the single crystal now extended into the smooth lines on the powder pattern.

Since only'd' can be measured from a powder pattern, all the information from the three-dimensional reciprocal lattice has thus been compressed into one dimension. Due to the complexity of such powder patterns it is usually very difficult to interpret them without further information.

Sample size should be about 5 to 10 micron to eliminate line broadening or extinction effects [1]. Depending on the type of crystal structure and crystal parameters intense peaks are developed at different θ corresponding to different atomic planes [2,3]. A typical XRD pattern of spinel ferrite structure is as shown in Figure 3.3. X-ray diffraction can also be used for determination of crystal structure from the peak broadening technique. It is known that, as the particle size reduces the number of diffraction centers is reduced and the peak is broadened. By using Sherrer [4] equation average crystallite size can be found out considering the most intense peak. The Sherrer is given as

$$D = 0.9\lambda \, / \, \beta\cos\theta \qquad (3.4)$$

Where D is the average crystalline size, λ is the X-ray wavelength used, β the angular line width of half maximum intensity and θ the Bragg angle in degrees.

Using XRD patterns lattice constant and X-ray density is evaluated using the following relation.

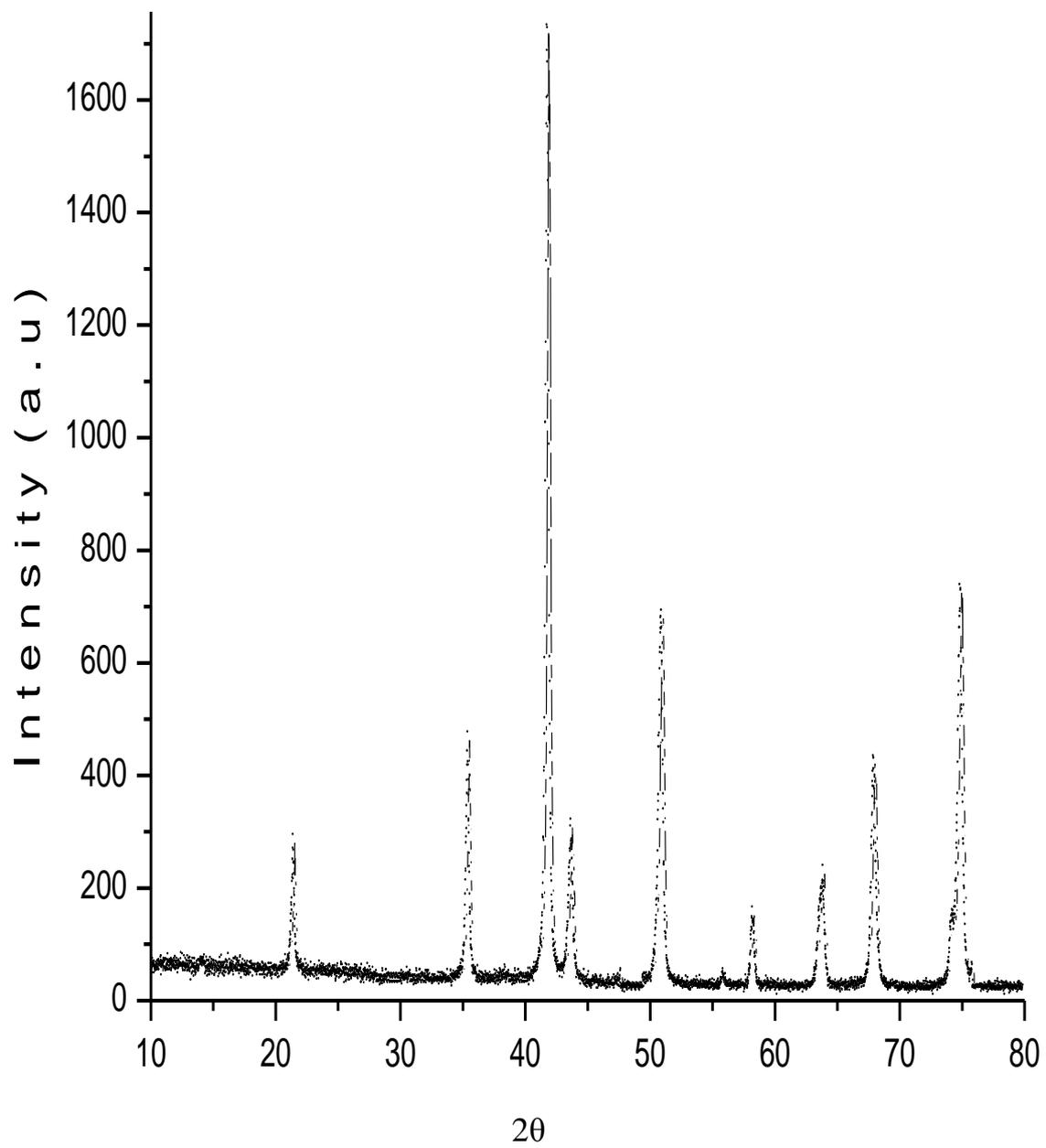$$a = \, d \, \sqrt{N} \qquad (3.5)$$

where $N = h^2 + k^2 + l^2$

$$dx = 8M/Na^3 \qquad (3.6)$$

where M = molecular weight of each sample

a = lattice parameter

N = Avagadro number = 6.023×10^{23}

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Figure 3.3: A typical XRD pattern of spinel ferrite structure

3.2 Fourier Transform Infrared Spectrometer

The Fourier transform is a mathematical manipulation, which relates a signal, curve or algebraic function to its frequency content. In Fourier spectroscopy the output signal is known as interferogram and is produced by an interferometer. The frequency content curve is simply the conventional spectrum i.e. intensity plotted vs wavelength or frequency.

The interferogram and spectrum contain the same information but rearranged. The Fourier transform breaks down the interferogram into a set of sine waves, which represent the individual wavelength components making up the light. The set of sine waves is then ordered in terms of wavelength to produce conversion spectrum [5].

To find the structural changes taking place in combustion reaction the IR spectra in the range $450 - 4000$ cm^{-1} were recorded using a Fourier Transform Infrared Spectrometer (Perkin Elmer FT-IR Spectrometer). The samples were mixed with spectral grade KBr as the standard, and then pressed to obtain circular discs of appropriate 1mm thickness. IR spectra are obtained by detecting changes in transmittance (or absorption) intensity as a function of frequency. Most commercial instruments separate and measure IR radiation using dispersive spectrometers or Fourier transform spectrometers.

The infrared region of the electromagnetic spectrum extends from 14,000 cm^{-1} to 10 cm^{-1}. The region of most interest for chemical analysis is the mid-infrared region (4,000 cm^{-1} to 400 cm^{-1}), which corresponds to changes in vibration energies within molecules.

The far infrared region (400 cm^{-1}to10 cm^{-1}) is useful for molecules containing heavy atoms such as inorganic compounds but requires rather specialized experimental techniques.

3.2.1 Use of the Technique

It is rarely, if ever, possible to identify an unknown compound by using IR spectroscopy alone. Its principle strengths are: (i) it is a quick and relatively cheap spectroscopic technique, (ii) it is useful for identifying certain functional groups in molecules and (iii) an IR spectrum of a given compound is unique and can therefore serve as a fingerprint for this compound.

3.2.2 Infrared Activity

Not all possible vibrations within a molecule will result in an absorption band in the infrared region. To be infrared active the vibration must result in a change of dipole moment during the vibration. This means that for homonuclear diatomic molecules such as Hydrogen (H_2), Nitrogen (N_2) and Oxygen (O_2) no infrared absorption is observed, as these molecules have zero dipole moment and stretching of the bonds will not produce one. For heteronuclear diatomic molecules such as Carbon Monoxide (CO) and Hydrogen Chloride (HCl), which do possess a permanent dipole moment, infrared activity occurs because stretching of this bond leads to a change in dipole moment (since Dipole Moment = Charge x Distance). It is important to remember that it is not necessary for a compound to have a permanent dipole moment to be infrared active.

In the case of Carbon Dioxide (CO_2) the molecule is linear and Centro symmetric and therefore does not have a permanent dipole moment. This means that the symmetric stretch will not be infrared active. However in the case of the asymmetric stretch a dipole moment will be periodically produced and destroyed resulting in a changing dipole moment and therefore infrared activity.

3.2.3 The Fingerprint Region

The fact that there are many different vibrations even within relatively simple molecules means that the infrared spectrum of a compound usually contains a large number or peaks, many of which will be impossible to confidently assign to vibration of a particular group.

Particularly notable is the complex pattern of peaks below 1500 cm^{-1}, which are very difficult to assign. However, this complexity has an important advantage in that it can serve as a fingerprint for a given compound. Consequently, by referring to known spectra, the region can be used to identify a compound.

3.2.4 Interpretation of Spectra

To obtain a more detailed interpretation of an IR spectrum it is necessary to refer to correlation charts and tables of infrared data. There are many different tables available for reference and a brief summary is given below for some of the main groups. When assigning peaks to specific groups in the infrared region it is usually the stretching vibrations, which are most useful. Broadly speaking, these can be divided into four regions:

3700 – 2500 cm^{-1} Single bonds to hydrogen

2300 – 2000 cm^{-1} Triple bonds

1900 –1500 cm^{-1} Double bonds

1400 – 650 cm^{-1} Single bonds (other than hydrogen)

It should also be noted that the region 1650 – 650 cm^{-1} contains peaks due to bending vibrations but it is rarely possible to assign a specific peak to a specific group.

3.2.5 Sample Preparation

There are different techniques that can be employed in the sample preparation depending in the physical form of the sample to be analyzed. As we have employed potassium bromide disk method, all discussions are concerned to this method only.

In potassium bromide disk method, Pellets are used for solid samples that are difficult to melt or dissolve in any suitable IR-transmitting solvents. The sample (0.5 to 1.0 mg) is finely ground and intimately mixed with approximately 100 mg of dry potassium bromide (or other alkali halide) powder. Grinding and mixing can be done with an agate mortar and pestle. The mixture is then pressed into a transparent disk in an evacuable die at sufficiently high pressure. Suitable KBr disks or pellets can often be made using a simpler device such as a Mini-Press. To minimize band distortion due to scattering of radiation, the sample should be ground to particles of 2 μm (the low end of the radiation wavelength) or less in size.

The IR spectra produced by the pellet technique often exhibit bands at 3450 cm^{-1} and 1640 cm^{-1} due to absorbed moisture [6].

3.3 Thermogravimetic and Differential Thermal Analysis (TG-DTA)

3.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is especially useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints.

3.3.2 Differential Thermal Analysis (DTA)

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature differential between the sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample, which lead to the absorption or evolution of heat, can be detected relative to the inert reference. Differential temperatures can also arise between two inert samples when their response to the applied heat treatment is not identical. DTA can therefore be used to study thermal properties and phase changes which do not lead to a change in enthalpy. A DTA curve can be used as a fingerprint for identification purposes.

DTA may be used formally as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

3.4 Transmission Electron Microscopy (TEM)

XRD gives the crystal structure and average crystallite size, Transmission Electron Microscopy (TEM) shows the particle morphology and its size distribution. A high voltage (120-200 Kev) finely focused electron beam is passed through a thin (50-200 nm) solid sample. Electrons scattering from atoms in the material derive contrast. Electrons undergo coherent scattering (diffraction) from lattice planes in crystalline materials yielding phase identification. Characteristic x-rays are produced and detected in a separate detector permitting qualitative elemental analysis. The diffraction pattern is produced on a fluorescent screen.

A typical TEM instrument has

    (a) Electron gun arrangement

    (b) Focusing arrangement

    (c) Arrangement to observe the image of the sample and electron diffraction.

Magnetic lenses are employed to achieve short focal lengths. The filament heats the needle – like cathode, which emits electrons thermionically. The beam passes through a hole (called a wehnelt cup), converges on the optical axis and crosses it. The beam is then accelerated by an anode and passed through a series of magnifying lens before it is projected on a fluorescent screen and recorded on a photographic plate.

The sample is usually covered with a conductive coating to enable it to discharge electrically.

3.4.1 Sample preparation for TEM analysis

The spinel ferrites we have prepared are in the powder form and in nanosize. It is known very well from the literature that, the nanosize particles have a tendency to agglomerate and creates obstruction in having a clear TEM photograph of the powder samples. When working with these nanosize particles extra care has to be taken to get the best visualization for accurate measurements and analysis. In our case we have used methanol and ultrasonicated for nearly 15 – 20 minutes. A small drop of well-dispersed suspension was put on carbon grid for obtaining the TEM photograph. A magnification of hundred thousand is needed for visualizing the nanoparticles of size 5 – 40 nm.

3.4.2 TEM size distribution

From the TEM photograph, we can directly see the particle morphology, and one can find out the grain size. XRD data gives the average crystallite size and no evidence about its distribution. TEM can be used to measure the individual particle size and to find the distribution in the powder sample. To find the single phase, or any other impurities in the powder sample both XRD and TEM data can be used. The particle size estimated from TEM is slightly greater than the particle size estimated from XRD. XRD gives the information pertaining to only the crystallite region and contribution from the amorphous phase does not arise, and TEM gives the complete picture of the nanograin size particles.

Thus by using TEM and XRD one can study the morphology, distribution and their particle size. In our present work we have used Philips CM-12 Transmission Electron Microscope (TEM). Typical TEM photograph is a shown in Figure 3.4.

200 nm
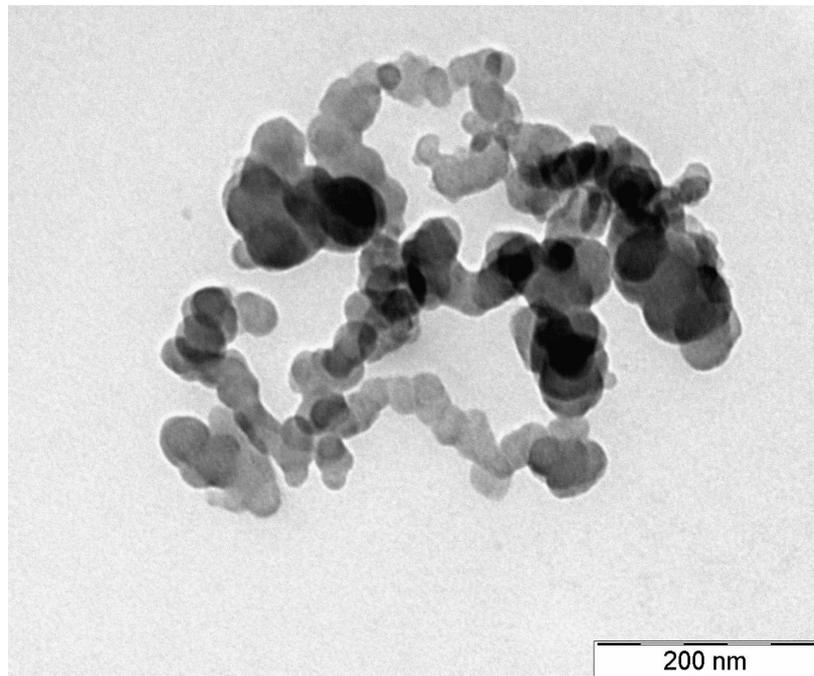
Figure 3.4: Typical TEM photograph

3.5 Magnetization Measurements

The Vibrating Sample Magnetometer (VMS), first developed by Foner in the late 1950s, is a basic research tool for determining magnetic properties in a variety of studies of the structure of paramagnetic, ferromagnetic, antiferromagnetic, diamagnetic and ferrimagnetic materials.

VSM's have been used in such areas as the study of amorphous and magnetic bubble domain materials and investigations of the nature of the bonds in intermetallic components. Further uses have included the measurement of hysteresis loops of magnetic tape and disc materials and the rare earth cobalt compounds. In addition, the VSM is ideal for superconductivity measurements (Meissner effect, diamagnetic shielding, and critical field determination) and the study of the magnetic properties of thin films or single crystals.

If any material is placed in a uniform magnetic field, a dipole moment will be induced in the sample proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample will induce an electrical signal in suitable placed stationary coils. This signal will be proportional to the moment, amplitude, and frequency of vibration. The material under study in the VSM is inserted in the sample holder so that it rests centered in a pair of pickup coils between the poles of an electromagnet. The sample holder is mounted using a sample rod in a transducer assembly which passes through the center of a driving coil. The transducer is driven by a power amplifier which itself is driven by an oscillator. The magnetic sample under study is constraint to vibrate only along the vertical axis. As it does so, it induces a signal in the sample pickup coils as described above. The magnitude of this signal is dependent on the magnetic properties of the sample itself. Attached to the sample holder rod is a permanent magnet.

A pair of stationary coils picks up the induced ac signal, which is proportional to the amplitude and frequency of the vibration and is used as a control signal for modulation of the transducer. The output of the sample coil is fed to the differential input of a lock-in amplifier. The reference input of the lock-in comes from the sine wave oscillator used to drive the sample holder. The output of the lock-in goes to the data acquisition computer as well as the magnitude of the applied magnetic field coming from a gauss meter. The signal from the lock-in amplifier is directly proportional to the magnetic moment of the sample. The computer is now able to plot the graph of the magnetic moment of the sample against the applied magnetic field.

In our present study the magnetic measurements were performed using the commercial PARC EG&G vibrating sample magnetometer VSM 4500. Magnetic hysteresis loops were measured at room temperature for different maximal applied magnetic fields up to 0.95T. Magnetic field sweep rate was 5 Oe/s for all measurements, so that the measurement of hysteresis loops with maximum field of 0.95T took about three hours to obtain hysteresis loops for measuring the magnetic properties. The samples prepared in powder form were fixed in paraffin in order to exclude the motion of powder in a measuring cap.

3.6 References

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