Chapter - 4

Synthesis and Characterization of ferrites

❖ Synthesis and characterization of hexaferrite samples:

This chapter comprises description of Strontium hexaferrites synthesis using different chemical routes. Synthesis materials were characterized by using different experimental techniques like DTA/DSC-TGA, FTIR, XRD, SEM, VSM and Dielectric measurements.

4.1 Sample preparation

Series 1: SrFe$_{12}$O$_{19}$ hexaferrites sample using co-precipitation, micro-emulsion and SHS methods.

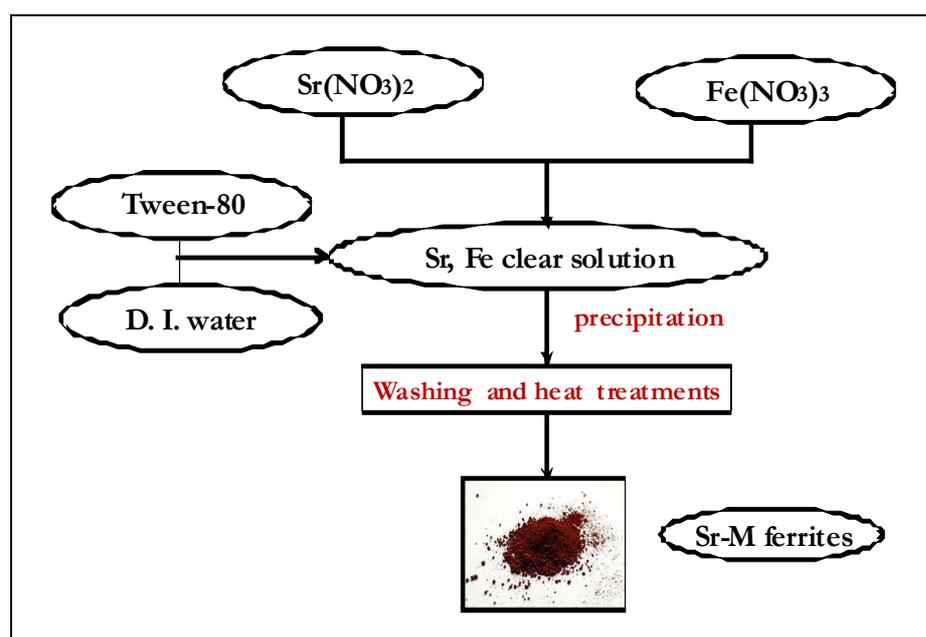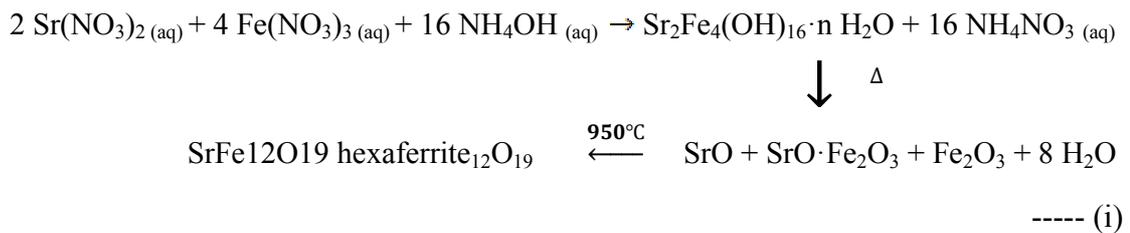**(i) A co-precipitation method (with and without non-ionic surfactant Tween-80)**

Figure 4.1 Schematic representation for the formation of SrFe$_{12}$O$_{19}$ hexaferrite using a co-precipitation method

SrFe$_{12}$O$_{19}$ hexaferrite particles were prepared using a chemical co-precipitation method. All starting chemicals were of high purity AR Grade and used without further purification. Starting materials; Strontium Nitrate, Sr(NO$_3$)$_2$ (*loba chem.*, 99 % pure) and Ferric Nitrate, FeN$_3$O$_9$·9H$_2$O (*Sigma Aldrich*, > 98 % purity) are taken with Sr:Fe atomic ratio of 1:12 were dissolved in deionized water by

continuous stirring using a magnetic stirrer. Then, 25 % aqueous solution of precipitating agent NH_4OH (*Merck*, GR grade) was slowly poured into mixture of metallic salt solution and stirred for 2 h in order to control the crystallite size and homogeneity of the samples. Simultaneously pH value of the solution is measured. NH_4OH was added until pH comes to 11 and dark brown coloured precipitates formed. The prepared solution was kept 24 hours for aging and then the gelatinous precipitate was filtered and washed several times using deionized water until the pH value of the solution became neutral. The obtained powder was dried at 250° C for 24 hrs in air, and then sintered at an optimized temperature 950° C for 4 hrs in a muffle furnace with static air atmosphere. **Figure 4.1** represents the schematic diagram of preparation method.

The major chemical reaction involved in the precipitation route can be described stepwise as follows:

$$2\ Sr(NO_3)_{2\ (aq)} + 4\ Fe(NO_3)_{3\ (aq)} + 16\ NH_4OH_{\ (aq)} \rightarrow Sr_2Fe_4(OH)_{16}\cdot n\ H_2O + 16\ NH_4NO_{3\ (aq)}$$

$$\downarrow \Delta$$

$$SrFe12O19\ hexaferrite_{12}O_{19} \xleftarrow{950°C} SrO + SrO\cdot Fe_2O_3 + Fe_2O_3 + 8\ H_2O$$

----- (i)

In order to study the effect of non-ionic surfactant Tween-80 (*s. d. fine chem.*, LR grade) in the crystallization of $SrFe_{12}O_{19}$ hexaferrite, the sample was prepared in presence of the surfactant. 0.01 M solution of Tween-80 was prepared to make an aqueous surfactant. A stoichiometric amount of metal salts (Strontium Nitrate and Ferric Nitrate), were dissolved in the prepared aqueous surfactant solution and stirred vigorously. Next steps are same as previous one, without surfactant. The solution was precipitated with NaOH, aged and then the precipitated were filtered, washed and dried.

The obtained precursors were divided into two parts. One part is conventionally sintered at 950° C for 4 hrs in muffle furnace and second part is heated under microwave frequency (2.45 GHz, Power 900 W) in a commercial microwave oven (make LG, model MC-767W/WS) for 30 minutes in order to optimize the sintering conditions.

(ii)   A microemulsion method

A novel method using water-in-oil (W/O) microemulsions has been successfully employed to obtain homogeneous ultrafine particles of controlled size of a variety of materials [1-3].

In this method, a surfactant [S] is dissolved in organic solvents which form spheroidal aggregates, named reverse micelles. It is known that the reverse micelles are in fact a water-in-oil microemulsions where tiny droplets of water are surrounded by surfactant molecules forming a so called "water pools", which are characterized by water-surfactant molar ratio, $w = [H_2O]/[S]$. Water pools of these reverse micelles act as micro-reactors for the synthesis of ferrite powders, in which the particles size of the product is controlled by the size of these pools [4].

Experimental procedure

Strontium hexaferrite, $SrFe_{12}O_{19}$ nanoparticles have been prepared with precipitation in water-in-oil microemulsion system, using iron sulphate and strontium nitrates in molar ratio 1/12 as starting materials.

A phase diagram [5] of water/CTAB/n-hexanol as shown in **Figure 4.2** was used in order to select proper composition of oil phase, surfactant and water containing metal salts.
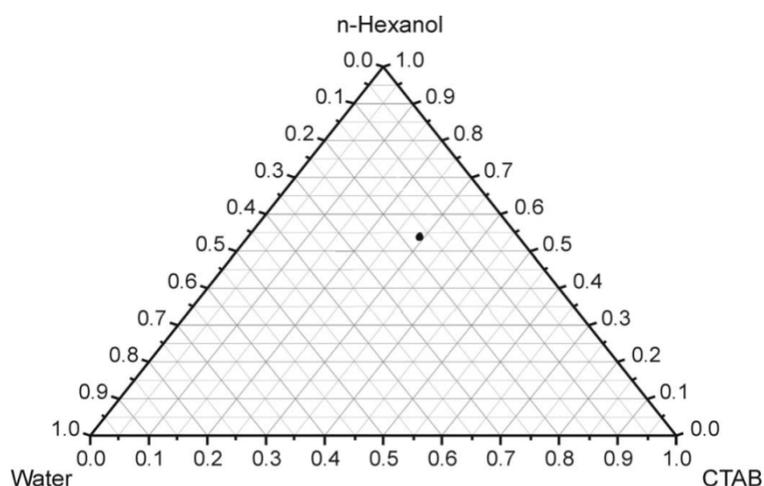

Figure 4.2 Phase diagram for proper composition of water/n-hexanol/CTAB

The microemulsion system consisted of n-hexanol as an oil phase, n-hexadecil trimethyl ammonium bromide (CTAB) as a surfactant and an aqueous phase of metal salts. Aqueous solution containing Fe^{2+} and Sr^{2+} ions was prepared by dissolving an

appropriate amount of metal salts, 1.2 M $FeSO_4$ (*Molychem*, GR grade) and 0.1 M $Sr(NO_3)_2$ (*loba chem.*, 99 % pure) in deionized water which resemble to the ferrite stoichiometry. Aqueous solution of 6N NaOH (*Merck*, 97 % purity) served as a precipitating agent. The composition of water : CTAB : oil as shown in the phase diagram (**Figure 4.2**) was taken as 14.3 : 30 : 55.7 wt % by mixing of an appropriate amount of water solution of metal salts with proper amounts of CTAB (*Spectrochem*, AR grade) and n-hexanol (*s. d. fine chem.*, LR grade). During mixing, the microemulsion was heated and kept at temperature between 50 and 60° C. When an alkaline solution of 6N NaOH was added to the starting microemulsion, the pH value rose to about 11 and green coloured intermediate precipitate was formed. As oxidation with H_2O_2 took place; intermediate precipitate was changed into the brownish precipitate of the final phase. A 30% solution of hydrogen peroxide, H_2O_2 was used as the oxidizing reagent. The resulting microemulsion was then mixed with an equal volume of water-methanol (1:1) solution to break up the micelles by washing the particles. The samples were centrifuged with ethanol for 20 min. in REMI Centrifuge (C-852, speed 3000 rpm) followed by further washing this particles several times using distilled water and dried at 100° C. The dried precursors sintered at 500°C in a muffle furnace for 2 hrs. Also one part of the powder is heated inside a microwave oven for 30 minutes. Schematic of the experimental procedure is shown in **Figure 4.3**.
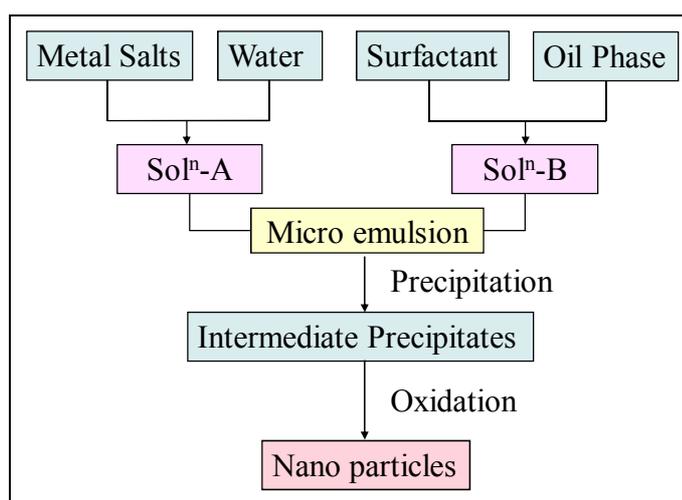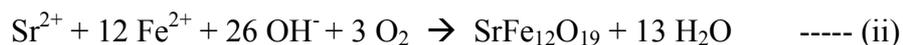

Figure 4.3 Schematic representation for preparation of nano particles
via micro emulsion route

The ionic reaction can be explained as:

$$Sr^{2+} + 12\,Fe^{2+} + 26\,OH^- + 3\,O_2 \;\rightarrow\; SrFe_{12}O_{19} + 13\,H_2O \qquad \text{----- (ii)}$$

The process of formation of the Sr-M hexaferrite by hydrolyzing and oxidizing of alkaline $Fe(OH)_2$ suspensions mixed with Sr^{2+} ions at elevated temperatures is based on the Schikorr's reaction [6]. In this experiment the reaction proceeds in "water pools" provided by a reverse micelle technique and is governed by the oxidation of hydrolyzed mixture of an appropriate composition in an alkaline media.

(iii)   A Self propagating high temperature Synthesis (SHS) route

Self propagating high temperature Synthesis (SHS) route also known as auto-combustion synthesis route using a fuel is a versatile method for the synthesis of a variety of solids [7]. The fuel used may be glycine, citric acid or urea. The main advantage of using this technique is due to the simplicity, the broad applicability range, the self-purifying feature due to the high temperatures involved, the possibility of obtaining products in the desired size and shape. This method is rapidly emerging as one of the most-convenient methods for the preparation of oxide materials. An aqueous solution of a redox system constituted by the nitrate ions of the metal precursor, acting as an oxidizer, and a fuel is heated up to moderate temperatures and, upon dehydration, the strongly exothermic redox reaction develops, which is generally self-sustaining and provides the energy for the formation of the oxide. Among the various wet chemical processes, the combustion route is cost effective for the synthesis of homogeneous, very fine, crystalline nano powders without the intermediate decomposition and/or calcinations steps which other conventional synthesis routes would require.

The characteristic feature of the SHS is, after initiation locally, the self-sustained propagation of a reaction wave through the heterogeneous mixture of reactants. The temperature of the wave-front can reach quite high values (2000-4000 K). The SHS mode of reaction can be considered to be a well-organized wavelike propagation of the exothermic chemical reaction through a heterogeneous medium, followed by the synthesis of desired condensed products.

Major physicochemical processes occurring during combustion synthesis

The following physicochemical processes affecting structure formation during combustion synthesis can be indentified:

1. Heat transfer from the reaction zone to unreacted particles in the mixture ahead of the reaction front

2. Phase transitions of solid reactants

3. Formation of eutectic melts and contact melting

4. Melting of reactants

5. Spreading of a molten phase under the action of capillary forces and due to the reduction of surface tension

6. Coalescence of fused particles

7. Gasification of volatile impurities and reactants

8. Chemical reaction with initial product formation

9. Melting of intermediate products

10. Melt crystallization upon cooling

11. Crystal growth

12. Phase transitions in solid products during cooling

13. Ordering of the crystal structure

The first nine processes proceed during the rapid increase in temperature to a maximum at the combustion front and the last four take place behind the combustion front with a constant or gradual lowering of temperature. Therefore, dynamic methods of investigation providing *in situ* monitoring of fast processes with a short duration are necessary to describe adequately the first group of synthesis steps during rapid heating. On the other hand, methods that analyze quenched reaction waves or final products can be applied to the study of the processes occurring during cooling (processes 10-13).

Experimental Procedure

Strontium hexaferrite was prepared by a novel combustion method using citric acid as the fuel. The starting materials used for the synthesis of $SrFe_{12}O_{19}$ hexaferrite

by SHS route are $Sr(NO_3)_2$ and $FeN_3O_9 \cdot 9H_2O$ solutions with a certain concentration level. Citric acid, $C_6H_8O_7$ (*Merck*, GR grade) used as a fuel.

Precursor was prepared in aqueous solution from metal nitrates and citric acid. Nitrate solution contains 0.1 M $Sr(NO_3)_2$ and 1.2 M $FeN_3O_9 \cdot 9H_2O$ dissolved separately in deionised water. Both the solutions were then properly mixed in a beaker. Citrate/nitrate ratio is taken as 1. The appropriate amount of citric acid was then added to the above solution and the mixture was stirred until complete dissolution occurred. Prepared mixture was heated and evaporated on a hot plate with stirring until it became a dark viscous resin. Continuous heating leads to the auto-ignition of dried resin with the evolution of large quantities of gases. The dark brownish colour ash obtained after combustion was analyzed for hexaferrite $SrFe_{12}O_{19}$ phase.

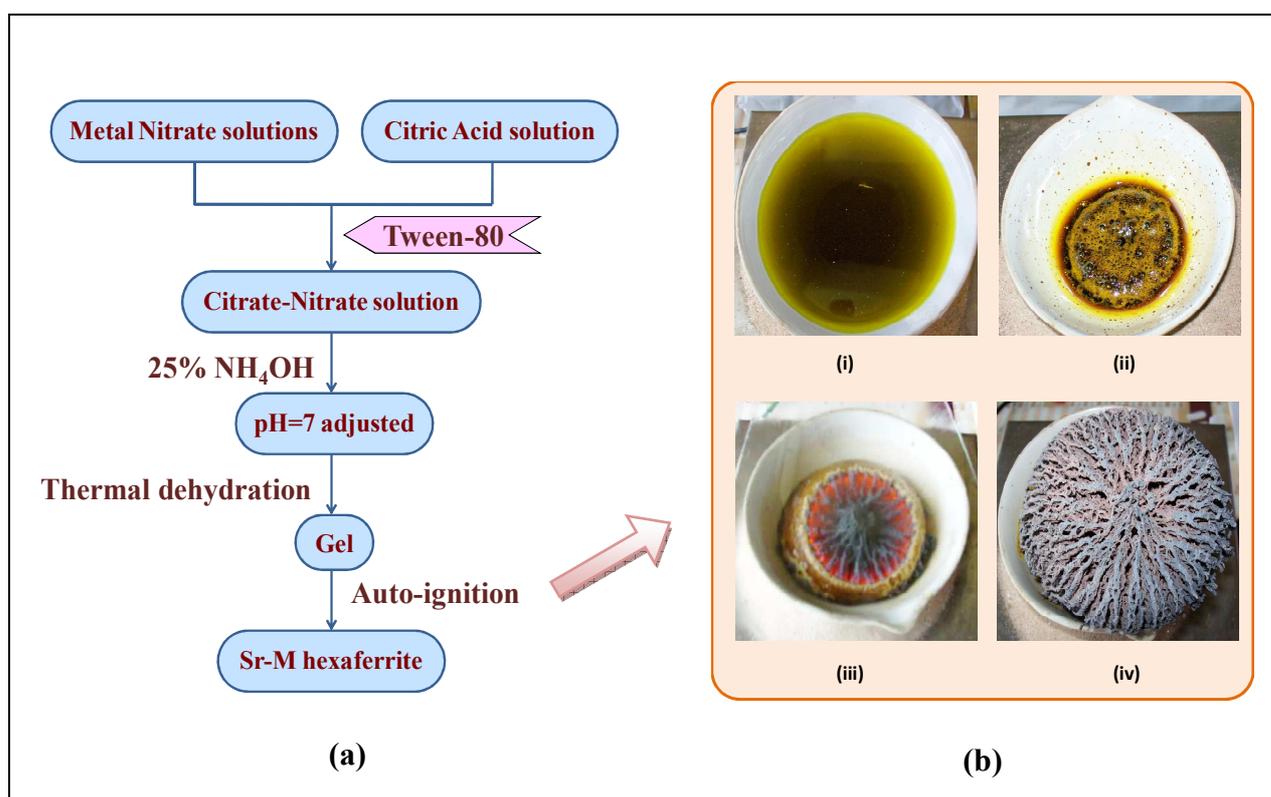**Figure 4.4 (a)** schematic flow-chart of SHS route to prepare $SrFe_{12}O_{19}$ hexaferrite and **(b)** sequential auto-ignition process represents: **(i)** solution after addition of NH_4OH, **(ii)** viscous gel after thermal dehydration of solution, **(iii)** starting of ignition and **(iv)** complete combustion forms black-brown fluffy flower of Strontium hexaferrite

The whole process completed within 30 min, but the time between the actual ignition and the end of the reaction was less than 30 sec. After the combustion is over in open air, it is further heated for 5-10 minutes to allow complete combustion of material. Obtained powder was calcined by two different ways: (i) powder was pre-heated at 450° C for 4 hrs followed by final calcinations at 950° C and (ii) powder heated inside microwave oven at microwave frequency of 2.45 GHz for 10 minutes. **Figure 4.4 (a)** represents a schematic diagram of sample preparation and **Figure 4.4 (b)** represents the steps of ignition from solution to final stage of fluffy powder.

In order to study the effect of non-ionic surfactant Tween-80 in the formation of $SrFe_{12}O_{19}$ hexaferrite samples, sample was prepared using SHS route, but in presence of Tween-80. Aqueous solution of 0.1 M Tween-80 (*s. d. fine chem.*, LR grade) prepared in deionised water. The metal nitrates were dissolved in aqueous solution of surfactant Tween-80. Nitrate solution was mixed with citric acid solution and then 25 % NH_4OH was poured to adjust pH = 7. Prepared solution was heated for thermal dehydration followed by self ignition process.

The obtained powder calcined using two different methods: first the conventional heating in muffle furnace at 950 ºC (after pre-heating at 450 ºC) for 4 hrs and second heating at microwave frequency for 30 mins.

Safety condition

The auto-combustion reaction can be explosive, yielding a high flame which quickly propagates through the reactant mixture. Therefore, safety becomes more and more important when many grams of powder have to be prepared by SHS route. Moreover, if the combustion reaction is more explosive, more powder is displaced from the combustion beaker and the product is thus lost because some of the very fluffy powder flies away with the combustion gases. Although a 90% recovery of the powder can be attained.

Advantages of SHS route

Compared with conventional ceramic processing, the most obvious advantages of combustion synthesis are primarily:

1. The generation of a high reaction temperature which can volatilize low boiling point impurities and, therefore, result in higher purity products.

2. The simple exothermic nature of the SHS reaction avoids the need for expensive processing facilities and equipment.

3. The short exothermic reaction times result in low operating and processing costs.

4. The high thermal gradients and rapid cooling rates can give rise to new non-equilibrium or metastable phases.

5. Inorganic materials can be synthesized and consolidated into a final product in one step by utilizing the chemical energy of the reactants.

These advantages have intrigued researchers to become more active in exploring the combustion synthesis of new and improved materials with specialized mechanical, electrical, optical and chemical properties.

The details of sample codes, heating condition and surfactant used, are listed in **Table 4.1**.

Table 4.1 Codes given to the samples prepared by using different methods for Series 1

Sr. No.	Preparation method	Surfactant	Heating condition	Sample code
1	Co-precipitation	None	as-precipitated	CPN-r
2			Microwave	CPN-MW
3			950° C	CPN-950
4		Tween-80	as-precipitated	CPT-r
5			Microwave	CPT-MW
6			950° C	CPT-950
7	Micro emulsion	CTAB	as-prepared	ME-r
8			Microwave	ME-MW
9			500° C	ME-500
10	SHS	None	as-burnt	SN-r
11			Microwave	SN-MW
12			950° C	SN-950
13		Tween-80	as-burnt	ST-r
14			Microwave	ST-MW
15			950° C	ST-950

Series 2: SrFe₁₂O₁₉ hexaferrites with different calcinations conditions

SrFe$_{12}$O$_{19}$ hexaferrite synthesized by co-precipitation route (as described in detail for series 1-A) in presence of non-ionic surfactant Tween-80 were calcinated in a wide temperature range, starting from 250 °C to 1100 °C in a static air atmosphere. Some of the as co-precipitated sample was kept aside for a raw sample characterization like FTIR and DTA/TGA. The raw sample was then divided into few parts for calcinations at different temperatures. The samples were calcinated at temperatures 250° C, 650° C, 750° C, 850° C, 950° C and 1100° C for 4 hours each in automated micro processor based muffle furnace shown in **Figure 4.5 (a)**.

Also one part of the raw sample is heated under microwave frequency (2.45 GHz) in a commercially available microwave oven at power 900 W for 30 mins. A Microwave oven used for microwave sintering is shown in **Figure 4.5 (b)**.

(a)   **(b)**

Figure 4.5 Sintering equipments **(a)** Muffle furnace and **(b)** Microwave oven

The details of sample codes with heating condition are listed in **Table 4.2**.

Table 4.2 Codes given to the samples prepared for Series 2

Sr. No.	Preparation method	Surfactant	Heating condition	Sample code
1			650° C	CPT-650
2			750° C	CPT-750
3	Co-precipitation	Tween-80	850° C	CPT-850
4			950° C	CPT-950
5			1100° C	CPT-1100

Series 3: Composites of $CoFe_2O_4/SrFe_{12}O_{19}$ ferrites

Nano composites of hard ($SrFe_{12}O_{19}$) and soft ferrite ($CoFe_2O_4$) are prepared by the mixing of the individual ferrite powders at appropriate ratio and subsequent heat treatment. Initially the microstructure of the individual phases is controlled by suitable processing.

Cobalt ferrite and Strontium ferrite nanoparticles were prepared separately by using SHS route. Then the Cobalt Ferrite and the Strontium Ferrite were mixed in different ratios by weight e.g., 1:1, 1:2, 1:4, 1:8 and each mixture was heated at 450° C for 4 hrs followed by the final calcination at 950° C for 4 hrs in static air atmosphere. The detail of samples compositions with coding is given in **Table 4.3**.

Table 4.3 Compositions of spinel / hexa ferrites taken for series-3 with sample codes.

Sr. No.	Sample Codes	Ratio of Co/Sr	
		Wt % of $CoFe_2O_4$ spinel ferrite	Wt % of $SrFe_{12}O_{19}$ hexaferrite
1	SH10	100	0
2	SH11	50	50
3	SH12	33.33	66.67
4	SH14	20	80
5	SH18	11.11	88.89
6	SH01	0	100

The composites thus obtained were then individually characterized with different experimental techniques.

Series 4: Swift Heavy Ion (SHI) irradiation study on ferrites

In order to study the SHI irradiation effect on structural properties of prepared ferrites, the samples were irradiated with Ag^{16+} ions with different fluences at Inter University Accelerator Centre (IUAC), New Delhi, INDIA. The details of the samples irradiated are listed in **Table 4.4**.

Table 4.4 Samples used for SHI irradiation with ion fluences.

Sr. No.	Sample	Synthesis route	ion fluence
1	$SrFe_{12}O_{19}$	co-precipitation	1×10^{12} ions/cm^2
2	$SrFe_{12}O_{19}$	co-precipitation	1×10^{13} ions/cm^2
3	$SrFe_{12}O_{19}$	SHS	1×10^{12} ions/cm^2
4	$SrFe_{12}O_{19}$	SHS	1×10^{13} ions/cm^2
5	$CoFe_2O_4$	SHS	1×10^{13} ions/cm^2

Irradiation experiments were performed in high vacuum chamber, with typical vacuum maintained at 1×10^{-6} mbar after purity and structural conformation of all the prepared samples. The samples were irradiated in vacuum with 200 MeV Ag^{16+} ions with current ½ pnA with fluence of 1×10^{-12} and 1×10^{-13} ions/cm^2 using 15UD Pelletron accelerator.

The target in the form of thin layer of ferrite material having thickness of about 10 mg/cm^2 for irradiation experiments were prepared by spreading fine ferrite powders in a aluminium ring of 1 cm diameter on a thin aluminium sheet, and uniform thickness was achieved by fixing the powder using liquid GE Varnish for the irradiation. These Aluminium sheets were then fixed to the four sides of the copper ladder. Also the ferrite pellets were made to the required size as determined by using the SRIM-2003 software for the SHI irradiation experiments.

The projected range (R_p), electronic energy loss (S_e) and nuclear energy loss (S_n) of 200 MeV Ag^{16+} ions in all the compounds calculated using SRIM-2008. Outputs of SRIM calculations for a range of 10 MeV to 200 MeV are illustrated in **Table 4.5** and **Table 4.6** for $SrFe_{12}O_{19}$ and $CoFe_2O_4$ respectively.

Variations of S_e & S_n with energy and depth in sample ferrites are illustrated in **Figures 4.6** for the ion energy ranges from 10 keV to 10 GeV for $SrFe_{12}O_{19}$ hexaferrite and $CoFe_2O_4$ spinel ferrite.

Table 4.5 Output of SRIM calculation for $SrFe_{12}O_{19}$ Hexaferrite

```
========================================================================
         Calculation using SRIM-2006
         SRIM version ---> SRIM-2008.04
========================================================================

Disk File Name = SRIM Outputs\Silver in Sr-Fe- O

Ion = Silver [47] , Mass = 106.905 amu

Target Density =  3.8776E+00 g/cm³ = 7.0372E+22 atoms/cm³
======= Target  Composition ============
 Atom  Atom    Atomic        Mass
 Name  Numb   Percent      Percent
 ----  ----   -------      -------
  Sr    38    003.13       008.26
  Fe    26    037.50       063.11
  O      8    059.37       028.63
==================================
Bragg Correction = 0.00%
Stopping Units =   eV / Angstrom
See bottom of Table for other Stopping units
```

Ion Energy	dE/dx Elec.	dE/dx Nuclear	Projected Range	Longitudinal Straggling	Lateral Straggling
10.00 MeV	3.653E+02	5.037E+01	3.26 um	4162 A	4477 A
20.00 MeV	6.933E+02	3.076E+01	5.00 um	4888 A	5826 A
30.00 MeV	9.254E+02	2.270E+01	6.18 um	5186 A	6406 A
40.00 MeV	1.091E+03	1.820E+01	7.14 um	5355 A	6752 A
50.00 MeV	1.218E+03	1.529E+01	7.99 um	5503 A	6994 A
60.00 MeV	1.318E+03	1.324E+01	8.76 um	5617 A	7178 A
65.00 MeV	1.362E+03	1.243E+01	9.13 um	5666 A	7256 A
70.00 MeV	1.401E+03	1.171E+01	9.49 um	5711 A	7327 A
80.00 MeV	1.471E+03	1.052E+01	10.18 um	5831 A	7451 A
90.00 MeV	1.530E+03	9.567E+00	10.84 um	5936 A	7558 A
100.00 MeV	1.581E+03	8.783E+00	11.47 um	6031 A	7652 A
110.00 MeV	1.626E+03	8.126E+00	12.09 um	6118 A	7736 A
120.00 MeV	1.665E+03	7.568E+00	12.70 um	6199 A	7812 A
130.00 MeV	1.699E+03	7.087E+00	13.29 um	6274 A	7882 A
140.00 MeV	1.729E+03	6.667E+00	13.87 um	6345 A	7947 A
150.00 MeV	1.756E+03	6.298E+00	14.44 um	6412 A	8007 A
160.00 MeV	1.780E+03	5.971E+00	15.00 um	6476 A	8063 A
170.00 MeV	1.801E+03	5.678E+00	15.56 um	6538 A	8116 A
180.00 MeV	1.819E+03	5.415E+00	16.11 um	6597 A	8167 A
200.00 MeV	1.850E+03	4.959E+00	17.19 um	6797 A	8260 A

```
-------------------------------------------------------
Multiply Stopping by    for Stopping Units
------------------      ------------------
1.0000E+00              eV / Angstrom
1.0000E+01              keV / micron
1.0000E+01              MeV / mm
2.5790E-02              keV / (ug/cm²)
2.5790E-02              MeV / (mg/cm²)
2.5790E+01              keV / (mg/cm²)
1.4210E+00              eV / (1E15 atoms/cm²)
1.3108E-03              L.S.S. reduced units
========================================================================
(C) 1984,1989,1992,1998,2008 by J.P. Biersack and J.F. Ziegler
```

Table 4.6 Output of SRIM calculation for $CoFe_2O_4$ Spinel Ferrite

```
========================================================================
        Calculation using SRIM-2006
        SRIM version ---> SRIM-2008.04
========================================================================
Disk File Name = SRIM Outputs\Silver in Co-Fe- O

Ion = Silver [47] , Mass = 106.905 amu
```

Target Density = $4.3337E+00$ g/cm^3 = $7.7859E+22$ atoms/cm^3
======= Target Composition ========

Atom Name	Atom Numb	Atomic Percent	Mass Percent
Co	27	14.29	25.12
Fe	26	28.57	47.60
O	8	57.14	27.27

```
===================================
```
Bragg Correction = 0.00%
Stopping Units = eV / Angstrom
See bottom of Table for other Stopping units

Ion Energy	dE/dx Elec.	dE/dx Nuclear	Projected Range	Longitudinal Straggling	Lateral Straggling
10.00 MeV	3.971E+02	5.641E+01	2.96 um	3770 A	4062 A
20.00 MeV	7.615E+02	3.444E+01	4.55 um	4436 A	5302 A
30.00 MeV	1.022E+03	2.542E+01	5.62 um	4707 A	5830 A
40.00 MeV	1.208E+03	2.038E+01	6.49 um	4860 A	6144 A
50.00 MeV	1.350E+03	1.712E+01	7.26 um	4993 A	6363 A
60.00 MeV	1.463E+03	1.482E+01	7.95 um	5095 A	6529 A
70.00 MeV	1.557E+03	1.311E+01	8.61 um	5179 A	6662 A
80.00 MeV	1.635E+03	1.178E+01	9.23 um	5286 A	6774 A
90.00 MeV	1.702E+03	1.071E+01	9.82 um	5380 A	6870 A
100.00 MeV	1.760E+03	9.831E+00	10.39 um	5465 A	6954 A
110.00 MeV	1.810E+03	9.096E+00	10.95 um	5542 A	7029 A
120.00 MeV	1.854E+03	8.471E+00	11.49 um	5614 A	7097 A
130.00 MeV	1.892E+03	7.933E+00	12.02 um	5681 A	7159 A
140.00 MeV	1.926E+03	7.463E+00	12.54 um	5744 A	7217 A
150.00 MeV	1.956E+03	7.050E+00	13.06 um	5804 A	7270 A
160.00 MeV	1.982E+03	6.683E+00	13.56 um	5861 A	7321 A
170.00 MeV	2.005E+03	6.355E+00	14.06 um	5916 A	7368 A
180.00 MeV	2.026E+03	6.060E+00	14.55 um	5968 A	7413 A
200.00 MeV	2.059E+03	5.551E+00	15.53 um	6146 A	7496 A

```
-----------------------------------------------------------
Multiply Stopping by    for Stopping Units
-------------------     -----------------
```

Multiply Stopping by	for Stopping Units
1.0000E+00	eV / Angstrom
1.0000E+01	keV / micron
1.0000E+01	MeV / mm
2.3076E-02	keV / (ug/cm^2)
2.3076E-02	MeV / (mg/cm^2)
2.3076E+01	keV / (mg/cm^2)
1.2844E+00	eV / (1E15 atoms/cm^2)
1.1763E-03	L.S.S. reduced units

```
==============================================================
```
(C) 1984,1989,1992,1998,2008 by J.P. Biersack and J.F. Ziegler
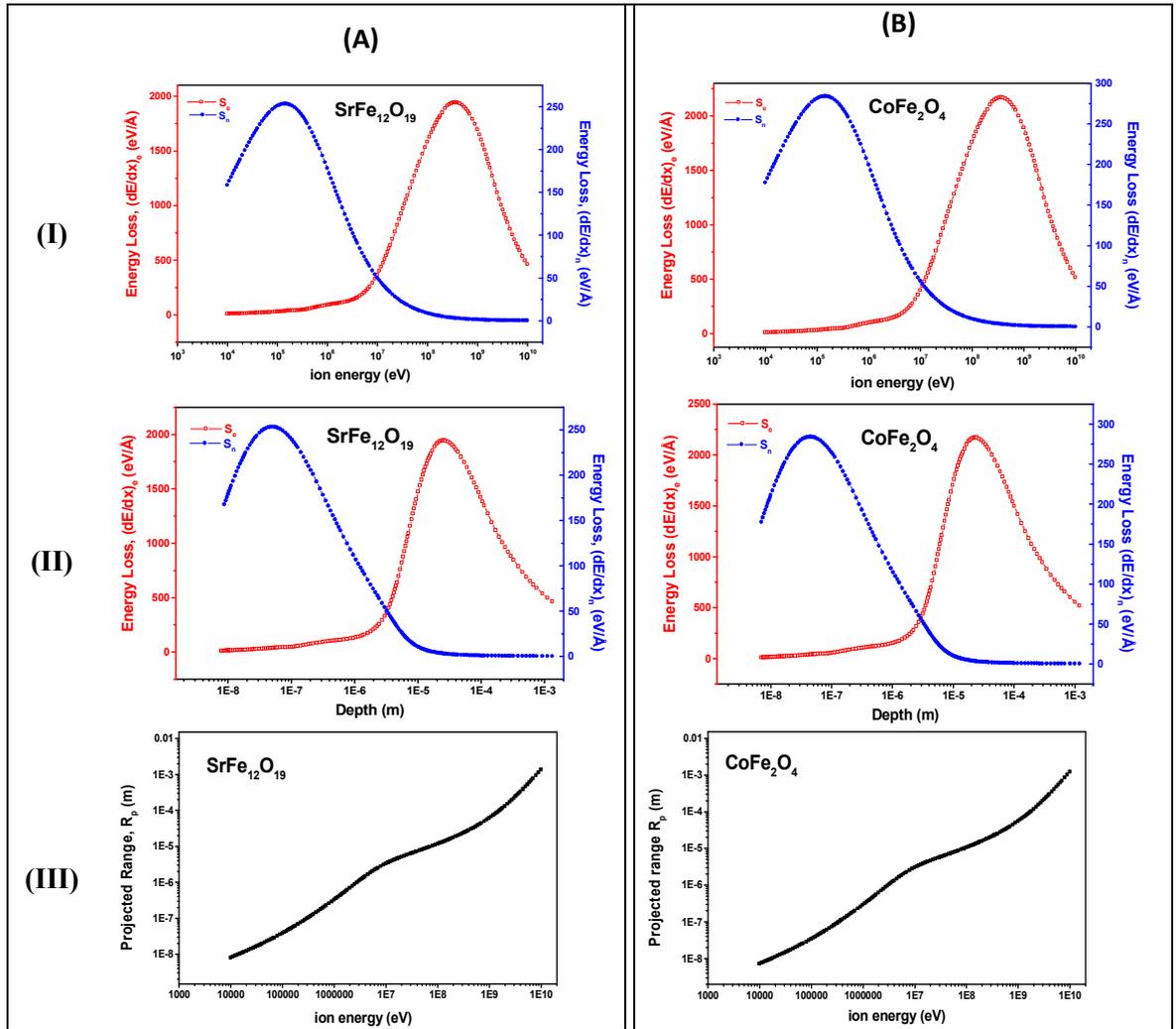
Figure 4.6 Ag^{16+} ions irradiation for (A) $SrFe_{12}O_{19}$ hexaferrite and (B) $CoFe_2O_4$ Spinel ferrite:

(I) electronic energy loss (S_e) and nuclear energy loss (S_n) versus log ion energy
(II) electronic energy loss (S_e) and nuclear energy loss (S_n) versus depth in ferrites
(III) Projected Range (**log R_p**) versus log ion energy

4.2 Measurements and Characterizations

The prepared series mentioned above were characterized by using different instrumental techniques and then analyze in order to study structural, thermal, morphology and magnetic and dielectric properties of the samples. The following techniques used for characterization:

4.2.1 DC Conductivity measurements

D. C. Conductivity measurements carried out in order to check the stability of chemical reaction during the sample preparation. DC conductivity of the reactions

was measured using **WELLTRONIX Digital Conductivity meter CM100** (as shown in **Figure 4.7 (a)**). It is a high quality precision instrument. Meter is designed for measuring the specific conductivity of solution using a conductivity cell ranging from 20 μS to 200 mS. It enables to measure the conductivity, without manual balancing and the specific conductivity is read directly on a digital panel.

Figure 4.7 (a) WELLTRONIX Digital Conductivity meter CM100 and **(b)** pH meter at physics department

Throughout the chemical reaction of sample preparation, DC conductivity is measured keeping the temperature of the meter similar that of the solution. Reason to measure the conductivity of the solution is to check whether the salts have been dissolved completely in the solution or not. With adding the salts to the solvent, the conductivity of the solution rises because of the free ions separated from the salts. After it gets completely dissolved, solution becomes saturated and the conductivity becomes constant.

Simultaneously, pH of the solution was also measured during the reaction. For pH measurements, **Electroquip pHCal** (shown in **Figure 4.7 (b)**) was used. Some of the reactions like precipitation occur at certain pH value. Also, to check the neutrality of the solution pH measurement is required.

4.2.2 Thermal properties

Thermal analytical methods are used to detect and measure the changes such as weight, enthalpy, and dimensions of the samples when subjected to heating from an initial lower temperature to higher temperature at a specific rate. The changes occur in the sample with increase in temperature are phase transition, melting, sublimation,

decomposition, oxidation or reduction, combustion, heterogeneous catalysis and combination. The most common measurements to study these changes are:

1. TGA (Thermo Gravimetric Analysis),
2. DTA (Differential Thermal Analysis) and
3. DSC (Differential Scanning Calorimetric).

Figure 4.8 Photograph of Linseis STA PT1600 used for TG-DTA

1. TGA

A change in the weight of a substance is recorded as a function of temperature or time [8] through TGA technique. TGA curve is affected by the particle size. For a particle size of smaller dimension, the decomposition takes place earlier, while with greater particle size, the decomposition takes place only at higher temperatures (between 600-700° C). TG curve is characteristic of given compound, since the chemical reactions occurring over a definite range of temperature are a function of molecular structure. The thermal stability of given compound can be determined at a higher temperature using TGA study. Instrument used for TGA/DTA is **Linseis STA PT1600 (TG — DTA/DSC)** as shown in **Figure 4.8**.

2. DTA

Differential Thermal Analysis is a technique for recording the temperature difference between the sample and a reference material against either time or temperature, while keeping both them in the identical environment of heating or cooling. In DTA, the test sample and reference material (normally alumina)

undergoes controlled heating, which is linear with time. When the sample undergoes any chemical or physical change, curve will show temperature difference (ΔT) between test sample and reference in the form of either exothermic or endothermic peak. The shape and size of the peak can give the information about the nature of the test sample. Physical changes usually result an endothermic peak, whereas chemical reactions, particularly of oxidation nature result exothermic peak.

3. **DSC**

In DSC, the energy required to establish a zero temperature difference between the sample and the reference material is measured as a function of temperature or time. When an endothermic reaction occurs, the energy absorbed by the sample is compensated by an increased energy input to the sample to obtain zero temperature difference. As this energy is equivalent to the energy absorbed in transition, direct calorimetric measurements of the energy transition are obtained. On the DSC curve, the abscissa indicates the transition temperature and the peak area measures the total energy transfer to or from the sample.

In the differential temperature control circuit, signals of the temperature sample and reference are compared. If no reaction takes place then the differential power input to the sample and reference heater is zero, but if the reaction takes place ($\Delta H \neq 0$), a differential power is given to heater and a signal proportional to this differential power is transmitted to the recorder pan. The integral of the peak so obtained gives the internal energy change of the sample.

4.2.3 Structural and morphological analysis

It is necessary for any synthesized material to check its structural properties and morphology. Different types of impurities, particle homogeneity, presence of unwanted organic/inorganic phases in the samples, phase formation can be analyzed through the characterization techniques listed below:

1. FTIR (Fourier Transform Infrared Spectroscopy)

2. XRD (X-Ray Diffraction)

3. SEM (Scanning Electron Microscopy)

1. **FTIR**

The FTIR spectra of all the compounds were recorded using an instrument Bruker Tensor, model 27 (**Figure 3.2 (b)**) in the pellet form at room temperature for wave-number ranges from 4000 to 400 cm^{-1}. Samples for FTIR must be dry during recording because moisture absorbs IR very strongly around 3600 cm^{-1}, which can appear in the FTIR output. The IR spectrum is obtained by using KBr pellet. This pellet is made up of a dry KBr mixed with a very less amount (~ 0.1 %) of sample pressed with a hydraulic press (**Figure 4.9**). This pellet is then placed into the path of IR beam and examined for its spectrum.

Figure 4.9 Photograph of Hydraulic Press used to make pellets

A Nernst lamp is used as an IR source, which is heated electrically to about 1500° C. A monochromator is used to obtain a thin beam of light of single wavelength. The analyzer picks up the signals passed through the sample and automatically provides the graph of wave number versus transmittance (%).

2. **X-ray Diffraction**

The phase analyses of prepared samples were supplemented by powder X-ray diffraction (XRD) studies. A computerized **Seifert XRD 3000 PTS** unit (**Figure 4.10**) was employed for collecting 2θ values of diffraction and the intensity of the diffraction peaks. Phase identification was executed using a powder X software. X-ray diffractorgrams are plotted with WinPLOTR-2006 software with FullProf_Suite. The details of the parameters involved in XRD studies are summarized in **Table 4.7**.

Table 4.7 parameters for XRD studies

Radiation type, Anode	Cu
Filter	Ni
λ Value used	1.5418 Å , Kα
X-ray operation	40 kV, 30 mA
λ discrim	Diffracted beam, monochromator
λ detector	Scintillation Count
Temperature	22 ± 2 °C
Range of 2θ	20° to 80°
Step size	0.05 ° 2θ
Count time	3.0 sec

Figure 4.10 Photograph of XRD unit used for characterizations

From the resultant X-ray diffraction data, XRD patterns are plotted for all the samples and indexed with powderX software. The lattice parameters (*a* and *c*), *h k l* planes, unit cell volume *V*, X-ray density ρ_x, porosity *P*, average grain size *B* can be determined using following formulae:

(i)   Bragg's law is, $\dfrac{2 \sin \theta}{\lambda} = \dfrac{n}{d}$ (4.1)

Where, *n* is the order of diffraction, *λ* is wavelength of the source, *d* indicates interplaner distance and *θ* is an angle between incident and reflected ray.

(ii)   Unit cell volume, *V* and Inter planar distance, *d* can be determined by,

For cubic, unit cell volume, $V = a^3$ and $\dfrac{1}{d^2} = \dfrac{h^2+k^2+l^2}{a^2}$ and   (4.2)

For hexagonal system, $V = \dfrac{\sqrt{3}}{2} a^2 c$ and $\dfrac{1}{d^2} = \dfrac{4}{3}\left(\dfrac{h^2+hk+k^2}{a^2}\right) + \dfrac{l^2}{c^2}$ (4.3)

(iii)   X-ray density can be calculated by using the formula,

$$\rho_x = \frac{FW \times Z \times 1.661}{V} \; if \; V \; is \; expressed \; in \; cm^3$$ (4.4)

Where, *Z* is the number of atoms per unit cell and *V* is unit cell volume.

(iv)   Porosity, $P = \left(1 - \dfrac{D}{\rho_x}\right) \times 100 \;\%$ (4.5)

Where, *D* is the bulk density and ρ_x is the x-ray density.

(v)   Average grain size can be determined by,

$$B = \frac{0.89\,\lambda}{\beta\,\cos\theta}$$

(4.6)

Where, λ is the wavelength of the source and β is Full Width at Half Maxima in radian of the peak at an angle θ.

3. Scanning Electron Microscopy (SEM)

SEM is used to study the structural morphology of the sample. It is used to form an image to give qualitative and quantitative information. An electron probe of diameter 1-10 nm carrying current of 10^{-10} to 10^{-12} A is formed at the specimen surface. Electrons from a thermionic or field-emission cathode are accelerated by a voltage of 1-50 kV between cathode and anode. **LEO 440i** SEM instrument (**Figure 4.11**); at Facilitation Centre for Industrial Plasma Technologies (FCIPT), IPR, Gandhinagar is used to take SEM images for all the samples.

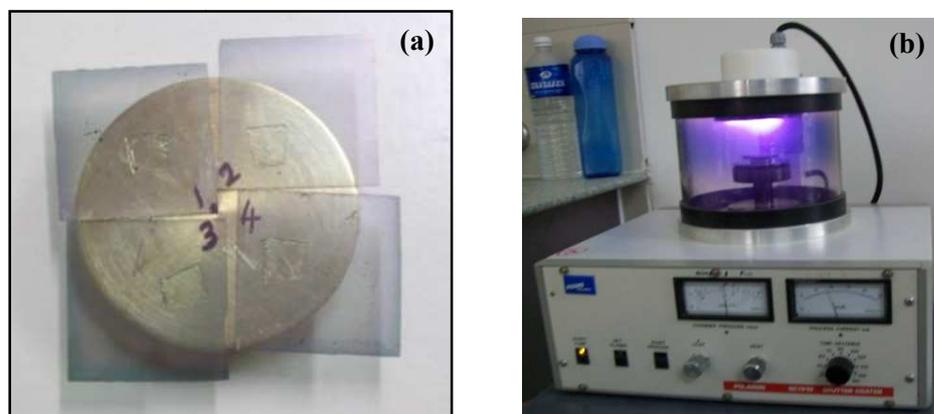**Figure 4.11** Photograph of LEO 440i instrument used for SEM

Figure 4.12 (a) A sample grid containing four samples, ready for sputtering **(b)** sputter coater

Specimen preparation is crucial for specimens to be examined under SEM as the specimen have to be occupied within the system vacuum and the incident beam is high voltage electron beam (of the order of thousands of Volts). The specimen (or its surface) must be electrically conductive and vacuum compatible.

Here, in case of ferrite powder samples, first they are sonicated with Acetone in ultrasonic bath in order to disperse the particles. After 10 min. of sonication, a drop of solution is taken over a glass slit (**Figure 4.12 (a)**) and then kept for drying for few minutes. Ferrites are basically non conducting materials. So they are coated with a thin (about 100-1000 Å) layer of gold to make the surface of samples conducting. This coating is applied to the specimen by plasma discharge techniques using POLARON SC7610 SPUTTER COATER (**Figure 4.12 (b)**). Sample grid after sputtering is then kept in a vacuum chamber for image observations. Some specifications during image recording are listed below:

Chamber pressure should be $10^{-5} - 10^{-6}$ Torr

Voltage between Cathode and Anode is 40 kV for highest resolution

Current passing through electron probe should be 100 pA for good resolution

4.2.4 Magnetic Properties

VSM (Vibrating Sample Magnetometry)

Magnetic measurement is a unique technique to get the information of domain wall motion, anisotropy, magneto-elastic coupling, magnetic hardness or toughness of magnetic material, magnetic ordering etc.

The magnetic measurements on hexaferrite samples were carried out by using high field hysteresis loop technique. The magnetic hysteresis loops (magnetization M vs. applied field H curves) for the samples were measured using a VSM instrument **EG & G Princeton Applied Research Instrument, model 4500** with a maximum field of 15000 Oe. Characterization is focused on mainly three parts: (i) Saturation magnetization M_s, the maximum magnetization attained by a magnetic system under the influence of external magnetic field, (ii) Coercive force or coercivity H_c, the force required to remove the residual magnetism from the material and (iii) Remanence

magnetization M_r, the magnetic flux density that remains in a material when the applied magnetic field is zero.

The sample in powder form is filled in a small tube made up of non-magnetic material. This tube is kept in a sample holder fixed at the end of a sample rod mounted in an electromechanical transducer, where this tube can vibrate freely. The transducer is driven by a power amplifier driven by an oscillator at a frequency of 90 Hz. The tube containing sample vibrates along the z-axis perpendicular to the magnetizing field. When the material placed in a uniform magnetic field between the poles of electromagnet, a dipole moment is induced and generates sinusoidal electrical signals which are recorded by the pickup coils, passed through lock-in, integrating amplifiers and finally gives the data in Digital Readout form.

4.2.5 Dielectric Properties

Dielectric parameters like, dielectric constant (ε), loss tangent (*tan δ*), and ac conductivity (σ_{ac}) are useful in determining the electrical properties of the material. Dielectric measurements of hexaferrites are carried out at room temperature to find variation of dielectric constant with frequency range 20 Hz to 2 MHz using **Agilent E4980A, Precision LCR meter** at department of Physics, Gujarat University, Ahmedabad.

Figure 4.13 A sample holder for dielectric measurement

Figure 4.13 shows a sample holder used for dielectric measurement for solid material. The powder samples are pressed with Hydraulic press to make the pellets. A record of the thickness and the diameter is done and then the parallel faces are painted with silver paste (*PD 3068, Arraycom India Ltd.*) to provide electrical contact. The sample is first inserted in the cell and the electrodes closed with the micrometer until they just touch the sample. The electrodes should not be forced against the sample. The micrometer is turned with a light finger touch and the electrometer setting recorded. The data were taken at room temperature.

The dielectric constants of samples can be determined using various equations as follows:

(i)   Capacitance of air, $$C_0 = \frac{\varepsilon_0 A}{t}$$ (4.7)

where, ε_0 = dielectric permittivity of free space = 8.854 x 10^{-14} Farad/cm

A = metalized area of one circular face, cm^2

t = thickness of the pellet, cm.

(ii)   Dielectric constant (real), $$\varepsilon' = \frac{C}{C_0}$$ (4.8)

(iii)   Dielectric constant (complex), $$\varepsilon'' = \frac{1}{2\pi f C_0 R_p}$$ (4.9)

(iv)   Loss tangent tan δ can found from equation,

$$\varepsilon'' = \varepsilon' \tan \delta$$ (4.10)

(v)   ac conductivity, $$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon'$$ (4.11)

LCR meter gives output data of ε' and ε''. From these, values of tan δ and σ_{ac} are calculated using equations 4.10 and 4.11.

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