

CHAPTER – 2

Experimental Details

2.1 Introduction

This chapter describes the synthesis procedure and the characterization techniques utilized. In the present investigations, the samples were prepared by microwave refluxing method. X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray Photoelectron Spectroscopy (XPS), Magnetic Property Measurement System (MPMS) and Mössbauer Spectroscopy were utilized for characterization of substituted magnetite nanoparticles.

2.2 Materials used for synthesis

For synthesis of various compositions, high purity raw materials were used. The specifications of these materials are listed in Table 2.1.

Table 2.1: Specifications of the materials used for the synthesis of substituted magnetite.

S.No.	Raw Materials	Chemical Formula	Purity (%)	Manufacturer
1.	Lithium Chloride	LiCl	99.99	Alfa Aesar
2.	Zinc Chloride	ZnCl ₂	97.9	Loba Chemi
3.	Aluminium Trichloride	AlCl ₃	98.0	Loba Chemi
4.	Hafnium Oxy Chloride	HfOCl ₂ .xH ₂ O	98.0	Alfa Aesar
5.	Ferrous Sulphate	FeSO ₄ .xH ₂ O	98.0	Loba Chemi
6.	Ferric Chloride	FeCl ₃	98.0	Loba Chemi
7.	Sodium Hydroxide	NaOH	98.0	Merck India

A few other solvents like Ethylene glycol etc. were also utilized to synthesize the samples.

2.3 Synthesis Method

In order to produce the substituted magnetite nanoparticles, microwave refluxing method was adopted.

2.3.1 Microwave refluxing method

The nanoparticles of $M_xFe_{3-x}O_4$ ($M = Zr, Hf, Al, Zn$ or Li and $0.01 \leq x \leq 1.0$) were synthesized using microwave refluxing technique. Initially, for preparing 8 g of final product of $M=Li, Zn, Al$ or Hf , substituted magnetite. The stoichiometric amounts of $LiCl, FeSO_4 \cdot 6H_2O$ and $FeCl_3$ or $ZnCl_2, FeSO_4 \cdot 6H_2O$ and $FeCl_3$ or $AlCl_3, FeSO_4 \cdot 6H_2O$ and $FeCl_3$ or $HfOCl_2 \cdot 8H_2O, FeSO_4 \cdot 6H_2O$ and $FeCl_3$ were dissolved in 100 mL ethylene glycol for different substitution. $NaOH$ pellets were added to this solution until pH of the solution reached to 12. The solution was then kept inside the microwave oven for 15 min with 2 min off and 5 min on position and the solution was irradiated to microwave. During the process, solution gets evaporated and enters into the condenser to get condensed. The process was carried for 15 min which produces the precipitate. The obtained precipitate was washed and then dried consequently for further characterization.

2.3.2 Preparation of ferrofluids

For the preparation of ferrofluids, initially substituted magnetite nanoparticles were dispersed in a solution of water (4 mL) and oleic acid (8 mL). This solution was then continuously stirred for 20 min at 60 °C. This provides homogeneous suspensions of nanoparticles which were found to be stable for few days. The concentration of the nanoparticles was 40 mg/mL for in ferrofluids except Zn substituted sample (42 mg/mL).

2.4 Characterizations Techniques

Following characterization techniques were employed to investigate the structural and magnetic properties of the substituted magnetite samples in the present thesis.

2.4.1 X-ray diffraction (XRD)

X-ray powder diffraction (XRD) patterns were obtained using a Philips X-ray diffractometer having CuK_α radiation ($\lambda=1.54056\text{\AA}$). Samples data were scanned in the range 20 to 80° with a scanning rate 2° min^{-1} at room temperature. The average crystallite size was estimated by using the most intense x-ray patterns peaks broadening employing Scherrer's formula.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2.1)$$

D is the average crystallite size, λ is the wavelength of the x-rays (1.54056Å), and θ and β are the diffraction angle and full-width at half maximum (FWHM) of the peak in the XRD pattern,

Bragg's law can be expressed as

$$(2d \sin\theta = n\lambda; \text{ where } n= 1, 2, \dots) \quad (2.2)$$

where n is known as the order of reflection.

2.4.2 Transmission Electron Microscopy (TEM)

The morphology and size distribution of the substituted magnetite nanoparticles were estimated using transmission electron microscopy (TEM, Technai-G² 200). In this technique, a beam of electron is transmitted to the ultra-fine specimen which interact with the specimen when passes through it. An image is formed during the interaction of electron transmitted through the specimen, it examined through CCD camera. The

powders having small quantity were dispersed in methanol using ultrasonic bath at room temperature. Two drops of the dispersed powders is put on the carbon coated copper grid and allowed to dry for 5 to 6 h before observing under TEM.

2.4.3 X-ray photoelectron spectroscopy (XPS)

The oxidation states of the elements Fe, Zr, Hf, Al, Zn and Li in the substituted magnetite were determined by a PHI5000 Versaprobe II photoelectron spectrometer (ULVAC-PHI) using an Al K_{α} X-ray beam. All the measurements were performed at pass energy of 50 eV. For the calibration of the absolute binding energy, the C-1s peak (284.5 eV) was used as an internal reference. The baseline was executed using a Shirley background function and the peaks were deconvoluted and quantified using XPSPEAK 4.1 software.

2.4.4 Magnetic Property Measurement System (MPMS)

The magnetic property measurements for tetravalent, trivalent, divalent and monovalent substituted magnetite nanoparticles were carried out using SQUID (MPMS-XL, Quantum Design) at room temperature with the field up to ± 2 tesla. For the determination of T_C the magnetization vs. temperature curves were collected for few samples.

2.4.5 Mössbauer Spectroscopy

All the Mössbauer spectra for as prepared $M_x\text{Fe}_{3-x}\text{O}_4$ ($M = \text{Zr, Hf, Al, Zn or Li and } 0.01 \leq x \leq 1.0$) samples were recorded in standard transmission geometry and in the stable acceleration mode (triangular waveform). ^{57}Co in Rh matrix at room temperature was used as a source. $\alpha\text{-Fe}$ was used as a standard to calibrate the spectrometer and isomer shift

values were estimated relative to it. The experimental data were fitted using a least squares curve fitting model.

2.5.8 Heating Efficiency

Heating ability for ferrofluid of substituted magnetite nanoparticles was measured with the Magnetherm 1.5 (NanoTherics) system. The measurements were carried out at various combinations of frequencies and amplitudes of AC magnetic fields. The temperature rise during MHT was observed by a copper-constantan thermocouple (T-type, NanoTherics, UK).

The specific absorption rate (SAR, Wg^{-1}) was estimated by employing the formula[47]:

$$SAR = \left(\sum_{i=1}^3 \frac{m_i C_i}{m_s} \right) \frac{dT}{dt}$$

where C_i was the specific heat capacities of materials e.g. for magnetite nanoparticles, $C_m = 0.937 \text{ Jg}^{-1}\text{K}^{-1}$, oleic acid, $C_o = 2.06 \text{ Jg}^{-1}\text{K}^{-1}$ and water $C_w = 4.186 \text{ Jg}^{-1}\text{K}^{-1}$. Similarly, m_i represented the mass of the materials, e.g. m_m , m_o and m_w were the mass of magnetite nanoparticles, oleic acid and water respectively. The dT/dt was the initial slope of the temperature vs. time curves at 30 °C.

