Appendix – I

Report of the work done

Project Title: "Development and Characterization of Co-Zn Ferrite Nanoparticles for Ferrofluid Applications."

i) Objectives of the Project:

1. Synthesis of nanostructed cobalt ferrite nanoparticles by co precipitation method.
2. Synthesis of nanostructured Co-Zn ferrite nanoparticles by co precipitation method.
3. Characterization of prepared samples.
4. Preparation of ferrofluid using the synthesized powder.
5. Study of properties of ferrofluid.
6. Conclusions or results.

ii) Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication

1. Initially the project related literature survey has been carried out before starting the actual experimental work of synthesizing the ferrite nanoparticles. For this different books and papers published in the referred journals were referred.
2. All materials are synthesized using facile chemical route.
   Variety of methods has been used for the synthesis of ferrite nanoparticles by researchers. These methods include sol-gel, hydrothermal, chemical co-precipitation, sonochemical reactions and ball milling. However, chemical co-precipitation method is relatively simple and provides good control over particle size hence particles with narrow size distribution can be obtained.

3. First of all magnetite; Fe_3O_4 [$Fe^{++}Fe2^{+++}O_4^{2-}$] was synthesized by co precipitation method and the formation of material was confirmed by XRD technique (Fig. 1).
4. After that the basic material needed; the cobalt ferrite ($CoFe_2O_4$), was synthesized by co precipitation method using relevant starting materials. The precursors used for preparation were: Cobalt (II) chloride ($CoCl_2$), Ferrous Chloride ($FeCl_2$), Ferric Chloride ($FeCl_3$). Aqueous solutions of the chemicals were prepared using double distilled water. The pH of the solution was adjusted to 7 to 8 by initially using Ammonia solution and later on using Sodium hydroxide (NaOH) and the results were better with ammonium hydroxide. The material was first characterized by XRD technique to check structure and phase formation of the material (Fig. 2).
5. Then the actual work of synthesizing the mixed ferrite; Co-Zn Ferrite particles was carried out using co precipitation method. Here pH for entire series was adjusted using Sodium hydroxide solution. Solution was added dropwise and pH was measured using pH paper. The mixed cobalt ferrite; $Co_{(1-x)}Zn_xFe_2O_4$ for x=0.1 to 0.9 in steps of 0.1 were synthesized via co-precipitation method.
6. The samples were characterized by XRD, VSM, SEM, EDS and FT-IR etc.
7. The work done is presented in various national and international conferences.
   (Reprints of presented papers attached)
8. And work is also published in an international journal
   (Reprint of published Paper attached).
9. The mixed ferrite synthesized (Cobalt Zinc ferrite) and ferrofluid prepared were presented at International Conference, at Pandharpur. It is published in Proceedings with (ISBN No.: ISBN 978-81-930740-0-8)
10. Some samples were sent for TEM analysis at SICART, Gujarat – the samples are sent back by SICART.
11. Samples were sent for characterization by TEM at Mumbai – the samples were sent back because the instrument was not working.
12. Co-Zn Fe_2O_4 is also synthesized-The XRD is shown for reference (Fig. 3).
13. The samples are also characterized by Mossbauer at pune.

14. The samples are also sent for a. c. susceptibility characterization at department of Geology, University of Pune - the result are awaited.

1) X –ray diffraction analysis:

As penetration depth of X-rays is more compared to electrons, the X-ray diffraction patterns obtained are characteristics of bulk material. The powders samples were characterized by X-ray diffractometer (XRD) technique to determine structural and phase investigations. The diffraction patterns show characteristic characteristics peaks for Fe_3O_4 with cubic structure (JCPDS No. 79-0418). The peaks were assigned the respective Miller indices (the seven peaks for ferrite)

The average crystallite size (D) is calculated using Debye Schereer relation:

$$D = \frac{k\,\lambda}{\beta \cos\theta} \qquad \ldots (1)$$

And the average crystallite size is about 10 nm suitable for ferrofluid preparation. The wavelength of X-ray radiation λ is 1.54056 Å. And β is the full width at half maximum (FWHM) of the diffracted peak; measured in radians. The angle of diffraction θ is measured in degree. The constant k is taken equal to 0.89; the constant k varies from 0.89 to 1.39. Fig. 1 shows the XRD patterns of Fe_3O_4 (magnetite) nanoparticles without any impurity phase. The value of lattice constant (d) was calculated using Bragg's condition for maximum of diffraction $2d \sin\theta = n\lambda$. Since for all peaks the order of diffraction is one, therefore n=1.The lattice parameter (a) is calculated using equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad \ldots (2)$$

to be $a = 8.35$ Å and it is in close agreement with the theoretical value reported $(a = 8.397$ Å$)$ in JCPDS No.22-1086. A XRD pattern obtained is shown for reference.

The strain is calculated using Williamson-Hall analysis and the material shows negligible strain.

The crystallite size of the particles is not generally same as the particle size due to the presence of aggregates. The strain

$$\epsilon = \frac{\beta}{4\tan\theta} \qquad \ldots (3)$$

From equations (1) and (3) , it was confirmed that the peak width from crystalline size varies as $\frac{1}{\cos\theta}$ and strain varies as $\frac{1}{\tan\theta}$.

Assuming that the particle size and strain contributions to line broadening are independent to each other and both have a Cauthy-line profile (positive slope with positive intercept), the observed line breadth is simply the sum of equations (2) and (3)

$$\beta = 4\epsilon\tan\theta + \frac{k\,\lambda}{D\cos\theta}$$

Multiplying throughout by $\cos\theta$:

$$\beta\cos\theta = 4\epsilon\sin\theta + \frac{k\,\lambda}{D}$$

This is W-H equations. A plot with $4\sin\theta$ along $x-$axis and $\beta\cos\theta$ along the $y-$axis is drawn. From the linear fit to the data, the crystalline size is estimated from the intercept, and the strain ϵ , from the slope of the fit. The crystallite size is estimated from the y-intercept,

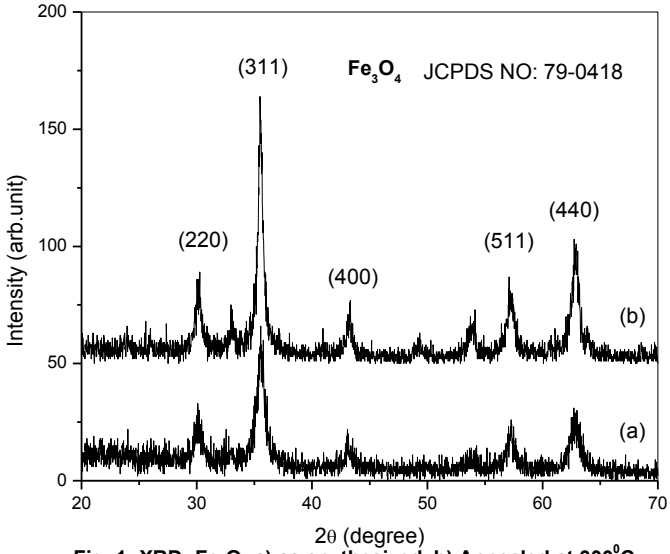

Fig. 1: XRD: Fe_3O_4 a) as snythesized, b) Annealed at 300^0C

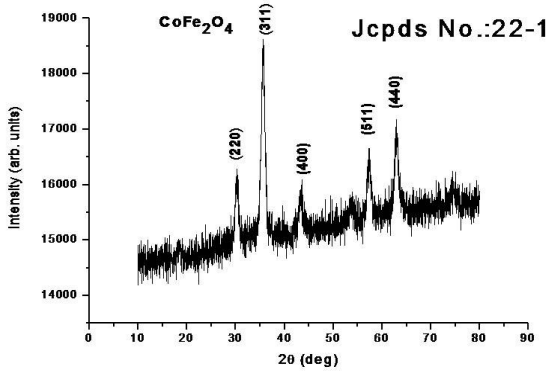

Fig.2: XRD of $CoFe_2O_4$

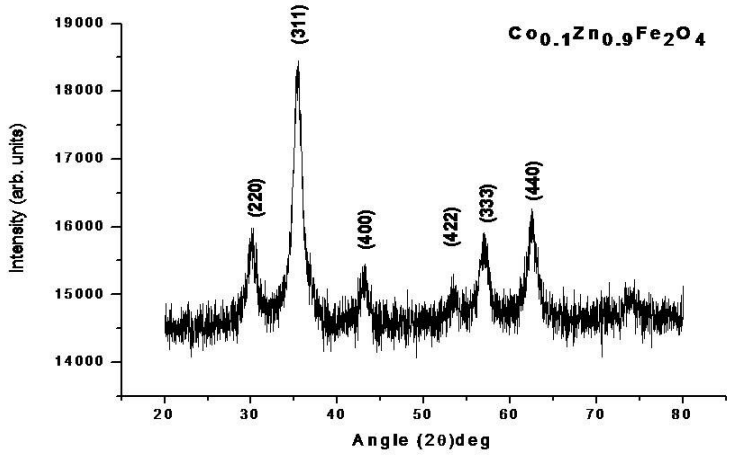

Fig. 3: Cobalt Zinc Ferrite – XRD

2) VSM analysis

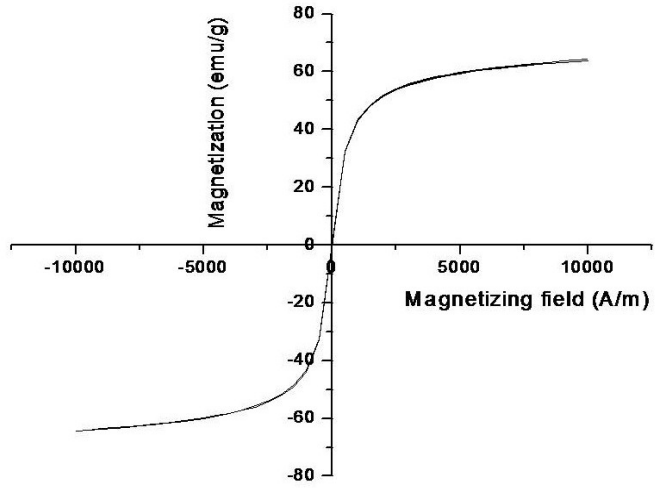

Fig. 4 Vibrating Sample Magnetomete-Superparamagnetic nat

The magnetic behavior was the nanoparticles was characterized by vibrating sample magnetometer. The magnetic measurements show supermagnetic nature of the sample. Whether the Particles are suitable for ferrofluid preparation or not is tested by D.C. magnetization; Vibrating Sample Magnetometer method (VSM). The particles exhibit zero coercivity and zero retentivity (or remanence) at room temperature which confirms Superparamagnetic nature of the sample. The Fig.4 is of VSM showing superparamagnetic nature of the particles. For preparation of ferrofluid the particles must be nanosized and superparamagnetic (nanoparticle size nearly 10 nm). The saturation magnetization is about 63 emu/gm. The value is high enough. Some of the samples show supeparamagnetic behavior. However, some samples show hysteresis as well. But the values of retentivity and corecivity for these samples are small.

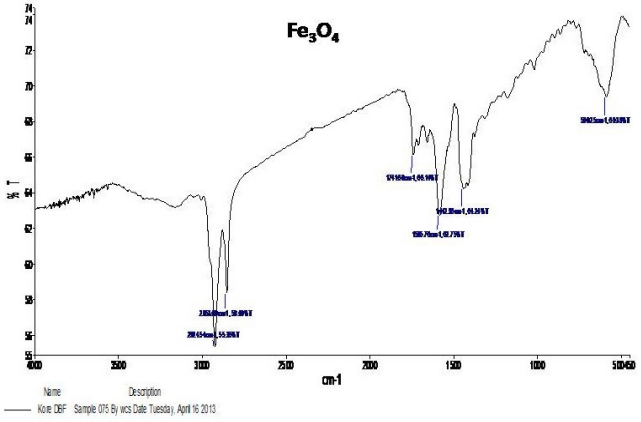

Fig. 5: FTIR – Fe_3O_4

3) FT –IR analysis

The Fourier Transform Infra-red (FT-IR) analysis was carried. The transmission peaks co nfirm the formation of material. A FT-IR graph is shown for reference (Fig.:5).

4) Ferrofluid preparation:

A ferrofluid is a suspension of magnetic particles of nanometer dimension in a carrier liquid. A ferrofluid is then synthesized using these supermagnetic nanoparticles with kerosene as a carrier liquid. The particles are coated with oleic acid to prevent

agglomeration. The prepared ferrofluid is found to be stable. The ferrofluid was prepared in kerosene.

5) SEM Characterization:

most common techniques used for the measurement of particle size rather than crystallite size is: i) Light scattering, ii) Scanning Electron Microscopy (SEM), and iii) Transmission Electron Micriscopy (TEM). Electrons do not penetrate matter as well as X-rays. So electrons diffraction effects result from penetration only to small depths in the material. Evidently surface layers would not be investigated by X-ray diffraction. In fact atoms scatter electrons more efficiently than X-rays. The scattering coefficient of electrons by atoms is much higher than that of X-rays. Hence electrons are preferred for structure investigations than X-rays.

Samples were characterized by Scanning Electron Microscope to get grain size. The

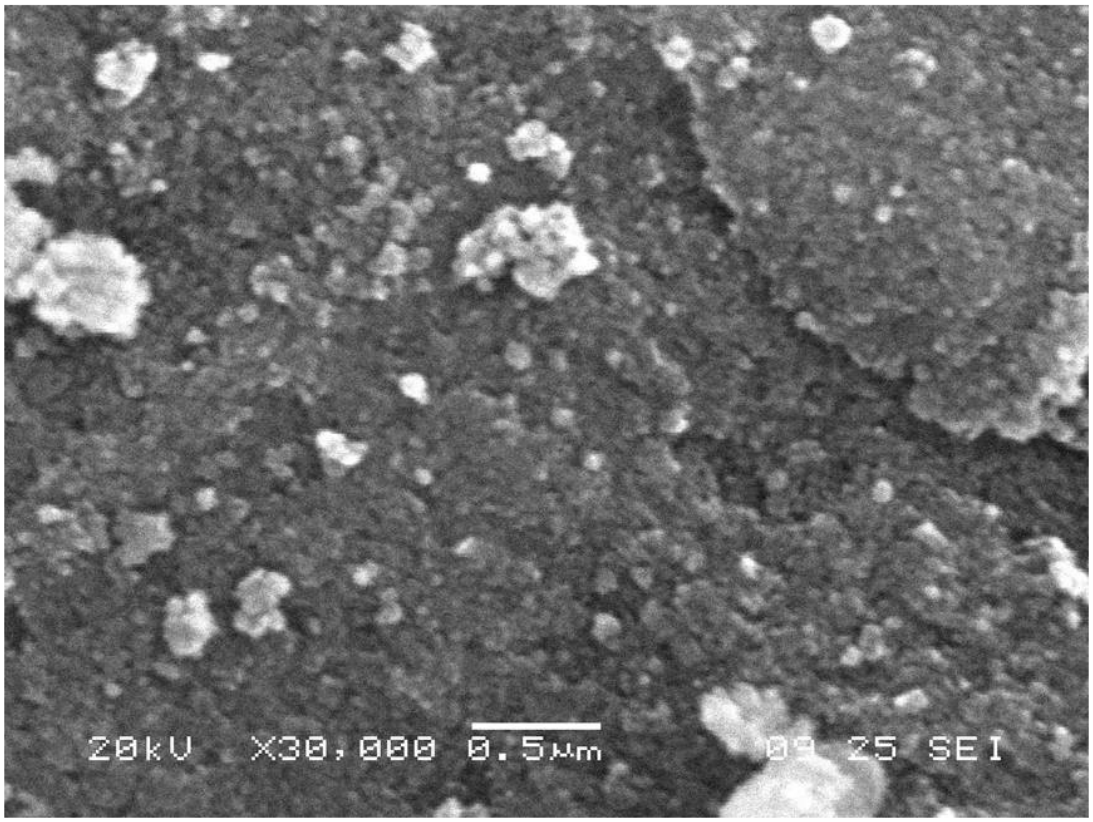

Fig. 6:SEM , SK4 : Cobalt Zinc ferrite $Co_{0.6}Zn_{0.4}Fe_2O_4$

grain size is in micrometers.

6) F

Papers presented and published

1) Papers Presented in – Workshop /Conference /Seminar /Symposia (Total: 04)

(INTERNATIONAL: 04)

Sr. No.	Title of the paper	Title of the Conference	Date	Organized by	Level
1.	NANOCRYSTALLINE Mn-Zn FERRITE PATICLES: SYNTHESIS AND MAGNETIC PROPERTIES.	2nd International Conference on "Emerging Trends in Chemical Sciences "(ETCS -2012)	2nd -4th Novemb er 2012	Dept of Chemical Science, Solapur University, Solapur.	International
2.	Development & Characterization of Superparamagnetic Zinc Ferrite Nanoparticles by Chemical Co-precipitation Route	International Workshop on Nanotechnology & Advanced Functional Materials (NTAFM 2013)	24,25 July, 2013	Material research society of India, Organized NCL, Pune .	International Workshop
3.	Ferrofluid : Properties and Applications	PHYSICS & CHEMISTRY OF ADVANCED MATERIALS (NCPACAM, 2013)	18th & 19th Decemb er, 2013	C.B. Khedgi's Basaveshwar Science, Raja Vijaysingh Commerce & Raja Jaysinh Arts College, Akkalkot, Solapur	National Conference (UGC Sponsored)
4.	Investigations on Superparamagnetic Cobalt ferrite ($CoFe_2O_4$)	International Conference on Functional Materials @ Nanoscale: Concerns and	9,10 & 11Mar. 2015	K.B.P. Mahavidyalaya, Pandharpur. Dist.Solapur	International conference

	nanoparticles. Abstract Published in Proceedings ISBN-978-81-930740-0-8	Challenges (ICFMNCC-2015)			

2. Publication of Research paper in International /National Journals

National Journal: 00 International Journal: **01** Total: 01

Sr. No.	**Title of the Paper**	**Journal**	**Level**	**Date**
1.	SYNTHESIS AND CHARACTERIZATION OF α-Fe_3O_4 NANOPARTICLES AND THIN FILMS	DAV International Journal of Science	International	(Volume-3 Issue-1 2014)