FINAL REPORT OF MINOR RESEARCH PROJECT

on

DEVELOPMENT AND CHARACTERIZATION OF SUPERPARAMAGNETIC FERRO-SPINELS

[F 47-1090/14(General/42/WRO) XII Plan]

(28th July, 2017 to 27th July 2019)

Submitted To

UNIVERSITY GRANTS COMMISSION

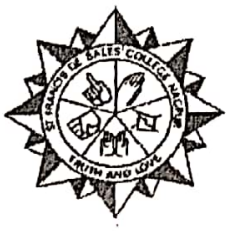
Western Regional Office(WRO)

Ganeshkhind Pune-411007

By

Mr. Halim Sagir Ahamad

Department of Physics,
St. Francis De Sales College, Nagpur



St. Francis De Sales College, Seminary Hills,
Nagpur -440006, M.S. (India)

Affiliated to Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur

2019

Annexure - III

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002
STATEMENT OF EXPENDITURE IN RESPECT OF MINOR RESEARCH PROJECT

1.Name of the Principal Investigator: **MR. HALIM SAGIR AHAMAD**

2.Dept. Of PI : **PHYSICS**

Name of College: **St. Francis De Sales College, Seminary Hills, Nagpur -440006, M.S. (India)**

3. UGC approval Letter No. and Date : **F 47-1090/14(General/42/WRO) XII Plan Dated 28 July 2017**

4. Title of research project : **Development and Characterization of Super-Paramagnetic Ferro-spinel**

5. Effective date of starting of the project: **28 July 2017**

6. a. Period of Expenditure: From **28 July 2017** to **28 July 2017**

b. Details of Expenditure _:

Sr. No.	Item	Amount Approved (Rs.)	Expenditure Incurred (Rs.)
i	Books & Journals	15000.00	15653.00
ii	Equipment	2,00,000.00	204284.01
iii	Contingency including special needs	25000.00	25621.10
iv	Field Work/Travel (Give details in the proforma).	10000.00	11850.00
v	Hiring Services	00	00
vi	Others	25000.00	29,471.00
vii	Chemicals & Glassware	00	14423.00
	Total Amount	**2,75,000.00**	**301302.11**

7. If as a result of check or audit objection some irregularly is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.

8. It is certified that the grant of Rs. **2, 75,000.00 (Rupees Two Lac Seventy Five Thousand** only) received from the University Grants Commission under the scheme of support for Minor Research Project entitled: **DEVELOPMENT AND CHARACTERIZATION OF SUPER-PARAMAGNETIC FERRO-SPINEL** vide UGC letter No. F. **47-1090/14(General/42/WRO) XII Plan dated 28 July 2017** has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions lay down by the University Grants Commission.

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

(Mr. Halim Sagir Ahamad)

PRINCIPAL

(Dr. K. T. Thomas)

Principal
St. Francis de Sales' College
Nagpur

For Kabra Sarda & Associates
Chartered Accountants
FRN:- 148295W

MRN 189652

CA. Darshan Kabra
Partner

KABRA SARDA & ASSOCIATES
Chartered Accountants

Head Office : S-Mart Super Bazar, Potegaon Road, Gadchiroli - 442 605.
Branch : 181, Gotmare Complex, Mezzanine Floor, Near Venus Book Depo, Gokulpeth, Nagpur - 440 010.
Ph. No. : +91 9421904434, 9096668886
E-mail : kabrasarda@gmail.com

Annexure - V

TO,
UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Utilization certificate

Certified that the grant of **Rs. 2,75,000.00 (Rupees Two Lac Seventy Five Thousand only)** received from the University Grants Commission under the scheme of support for Minor Research Project entitled ***DEVELOPMENT AND CHARACTERIZATION OF SUPER-PARAMAGNETIC FERRO-SPINEL*** vide UGC letter No. F. **47-1090/14(General/42/WRO) XII Plan** dated **28 July 2017** has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

SIGNATURE OF THE
PRINCIPAL INVESTIGATOR
(Mr. Halim Sagir Ahamad)

PRINCIPAL
(Dr. K. T. Thomas)
Principal
St. Francis de Sales' College
Nagpur

For KABRA SARDA & ASSOCIATES
FRN: 148295W

CA DARSHAN KABRA
PARTNER
MRN: 183652

KABRA SARDA & ASSOCIATES ★ FRN148295W ★ CHARTERED ACCOUNTANTS

ST. FRANCIS DE SALES COLLEGE ★ NAGPUR

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

~~Annual~~/Final Report of the work done on the Minor Research Project.

(Report to be submitted within 6 weeks after completion of each year)

1. Project report No. 1. /Final: **Final Report**
2. UGC Reference No : **F. 47-1090/14(General/42/WRO) XII Plan**
3. Period of report: 28 July 2017 to 27 July 2018
4. Title of research project : **Development and Characterization of Super-paramagnetic Ferro-spinel**
5. (a) Name of the Principal Investigator: **Mr. Halim Sagir Ahamad**

   (b). Deptt. : **Department of Physics**

   (c) College where work has progressed:

   St. Francis De Sales College, Seminary Hills, Nagpur -440006, M.S. (India)
6. Effective date of starting of the project: **28 July 2017**
7. Grant approved and expenditure incurred during the period of the report:
   a. Total amount approved Rs : **2,75,000.00**
   b. Total expenditure Rs.: **301302.11**
   c. Report of the work done: (Please attach a separate sheet):

      Separate Sheet Attached

7.c. Report of the work done

i. Brief objective of the project:

To develop the polycrystalline super-paramagnetic spinel ferrites by sol- gel auto-combustion method with urea as a fuel. And characterize the samples for super-paramagnetic behaviour

The proposed research work aims to synthesize nano-structured magnetic ferrite material. The synthesis will be done by undertaking suitable combinations of Ni, Cu, Mn; Co, Zn, Cd etc. in basic ferrite matrix (Fe3O4) by sol-gel microwave assisted auto-combustion method. The samples then will be investigated/characterized in detail for its physical, electrical and magnetic properties by X-ray Diffraction analysis, Scanning Electron Microscopy (SEM), Further, the magnetic properties like Magnetic Characterization will be undertaken by V.S.M study. Thus, this research work will be concerned to develop polycrystalline nano-particulate spinel ferrite materials with the enhanced properties, which may make it useful for applications in the field magnetic Hyperthermia for cancer diagnosis and other industrial applications.

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:

First Year

First, a detailed literature survey of the materials was conducted to choose the doping in the host matrix. The doping of Co^{2+} was selected in the mixed ferrite host material $NiCdFe_2O_4$ (Ni and Cd in Fe_3O_4) as it has not been studied in detail and its promising magnetic and dielectric properties in various applications in the field of magnetic hyperthermia and electromagnetic devices like multilayer chips (MLC). The Cadmium in Nickel ferrites decreases the magnetization. In order to achieve higher saturation magnetization with enhanced structural and electromagnetic properties Co^{2+} was selected as doping in $NiCdFe_2O_4$ with partial replacement of Cd^{2+}. A Simple and cost effective technique with promise of mass production of ultra-fine nano-ferrites by sol-gel microwaves auto-combustion technique employing urea as fuel was selected and the method results in polycrystalline nano-ferrites sample with superparamagnetic properties. Cadmium substituted Nickel Ferrite, $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ were successfully synthesized. The samples were then calcined at two different temperatures 600 °C and 800 °C and samples have been preserved / stored for the

further characterizations/analysis. The samples were sent for XRD, and FTIR study. After the results were obtained, the interpretation of the characterization was carried out. The XRD results were analysed with MDI Jade 5.0. FTIR results and XRD results indicated the formation of cubic spinel ferrites with space group $Fd\bar{3}m$ (227). Lattice parameter, Crystallite size, X-ray density, lattice strains in the samples were calculated from XRD results. It was observed that at higher calcinations temperature i.e. at 800 oC crystallite size were increased. Crystallite size from XRD results confirmed the formation of nano-ferrites. FTIR results indicated the formation of tetrahedral and octahedral lattices the FCC lattice. For quantitative elemental study samples were sent for FESEM characterization. And to study the magnetic characterization the samples were sent for the VSM study.

Second Year

FE-SEM images showed the nano-ferrites particles more or less agglomerated. The crystallite size observed from the SEM method is larger than the calculated from XRD method. It indicates each nano-particle consist of many crystallites and supports the agglomeration of nano-particles. To confirm the elemental composition of the samples after synthesis, energy dispersive x-ray spectroscopic (EDAX) analysis was conducted for the representative samples with x = 0.0, 0.02 and 0.05. The results confirm the stoichiometric presence of each element without loss of elements or presence of impurity. The magnetic study the samples were done by room temperature VSM analysis. The VSM results indicated soft ferrites nature of the samples with high saturation magnetization Ms. The Coercivity Hc and squareness ration (Mr/Ms) of the samples were found very small. The squareness ratio much smaller than 0.5 clearly indicated the uniaxial magnetocrystalline anisotropy of the samples and single domain (SD) nature of the nanoparticles. The small coercivity and squareness ratio and non-saturation of the samples at even at high applied magnetic fields suggested the most of the nanoparticles are superparamagnetic in nature. Research of the study were presented in an Internation conference and articles were wriited and communicated to the journals.

Research Paper Published :

a. Title of Paper "Structural properties of $Cu_xNi_{(1-x)}Fe_2O_4$ nano ferrites prepared by urea-gel microwave auto combustion method", H. S. Ahamad, N. S. Meshram, S.

B. Bankar, S. J. Dhoble & K. G. Rewatkar, (2017), published in 516:1, 67-73 ; ISSN: 0015-0193 (Print) 1563-5112 (Online)

DOI: 10.1080/00150193.2017.1362285

b. Article communicated to the journal "Ferroelectrics".

"Synthesis and study of Co doped Ni-Cd Ferro-spinels by Microwave Assisted Sol-Gel Auto-combustion Method"

The research ID for the same is 191125341.

c. Presented a paper on "Synthesis and Study of Superparamagnetic Ferro-Spinels by Microwave Assisted sol-gel Auto-Combustion Method" at International Conference on Multi-functional Advanced Materials ICMAM-2018 on 5-7th October, 2018, organized by Kamala Nehru Mahavidyalaya, Nagpur.

iii. Has the progress been according to original plan of work and towards achieving the objective. if not, state reasons:

The progress had been according to the original plan proposed.

iv. Please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to the concerned Regional Office of the UGC

Summary Report provided in the Final Report attached herewith

v. Any other information

NIL

SIGNATURE OF
THE PRINCIPAL INVESTIGATOR
(Mr. Halim Ahamad)

PRINCIPAL
(Dr. K.T. Thomas)
St. Francis de Sales College
Nagpur

(Seal)
ST. FRANCIS DE SALES COLLEGE ★ NAGPUR

Annexure – VII

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1.Title of the Project: **"Development and Characterization of Super-Paramagnetic Ferro-Spinel"**

2.NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR:

MR. HALIM SAGIR AHAMAD,
DEPARTMENT OF PHYSICS,
ST. FRANCIS DE SALES COLLEGE,
SEMINARY HILLS,
NAGPUR-44006

3.NAME AND ADDRESS OF THE INSTITUTION: **ST. FRANCIS DE SALES COLLEGE, SEMINARY HILLS, NAGPUR-44006**

4.UGC APPROVAL LETTER NO. AND DATE:

No. F. 47-1090/14(General/42/WRO) XII Plan dated 28 July 2017

5.DATE OF IMPLEMENTATION: **28 July 2017**

6.TENURE OF THE PROJECT : **Two Year (28 July 2017 to 27 July 2017)**

7.TOTAL GRANT ALLOCATED: **Rs.2, 75, 000.00 (Rupees Two Lac Seventy Five Thousand only)**

8.TOTAL GRANT RECEIVED: **Rs.2, 45, 000.00**

9.FINAL EXPENDITURE: **Rupees 3, 01, 302.11 (Rupees Three Lac One Thousand three Hundred Two and Eleven Paisa Only)**

10. TITLE OF THE PROJECT: "DEVELOPMENT AND CHARACTERIZATION OF SUPER- PARAMAGNETIC FERRO-SPINEL"

11.OBJECTIVES OF THE PROJECT:

i. To develop the polycrystalline spinel ferrites with superparamagnetic in nature by sol- gel microwave assisted auto-combustion method with urea as a fuel with particle size much smaller than 100 nm.

ii. To characterize the samples for super-paramagnetic behaviour and optimize the method so that synthesized nanoparticles have super-paramagnetic properties.

iii. It is proposed to synthesize the superparamagnetic nano-ferrites by undertaking suitable doping of Ni, Cu, Mn, Co, Zn, Cd etc. in basic ferrite matrix (Fe_3O_4) by sol-gel microwave assisted auto-combustion method. The samples then will be investigated / characterized in detail for its physical, electrical and magnetic properties. Further, the magnetic properties like Magnetic Characterization will be undertaken by V.S.M study. Thus, this research work will be concerned to develop polycrystalline nano-particulate spinel ferrite materials with the enhanced properties, which may will be useful for applications in scientific and technological applications like magnetic hyperthermia for cancer diagnosis and other industrial applications.

12.WHETHER OBJECTIVES WERE ACHIEVED: (GIVE DETAILS)

Yes,

i. First, detailed literature surveys of the materials were conducted to choose the doping in the host matrix. The doping of Co^{2+} was selected in the mixed ferrite host material $NiCdFe_2O_4$ (Ni and Cd in Fe_3O_4) as it has not been studied in detail and its promising magnetic and dielectric properties in various applications in the field of magnetic hyperthermia and electromagnetic devices like multilayer chip (MLC). The Cadmium in Nickel ferrites decreases the magnetization. In order to achieve higher saturation magnetization with enhanced structural and electromagnetic properties Co^{2+} was selected as doping in $NiCdFe_2O_4$ with limited replacement of Cd^{2+}.

ii. A Simple and cost effective technique with promise of mass production of ultra-fine nano-ferrites by sol-gel microwaves auto-combustion technique with

urea as fuel was selected and the method resulted in polycrystalline nano-ferrites sample with superparamagnetic properties. Cadmium substituted Nickel Ferrite, $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ were successfully synthesised.

iii. The synthesized samples were studied for their structural micro-structural, morphological studies and magnetic behaviour with XRD, FTIR, FEG-SEM and VSM in detail after calcinations at two temperatures 600 °C and 800 °C.

iv. The samples characterization confirmed the formation polycrystalline cubic nano-ferrites with cubic spinel structure with space group $Fd\bar{3}m$ (227) having superparamagnetic behaviour which was confirmed from the small coercivity (Near zero) and small squareness ratio as well as non-saturation of the samples at even at very high applied magnetic fields indicates that the most of the nanoparticles even if not all, are superparamagnetic in nature.

13.ACHIEVEMENTS FROM THE PROJECT:

The aim of the research module was to synthesize superparamagnetic polycrystalline mixed nano Ferro-spinel by sol-gel microwave assisted auto-combustion method. The synthesized nano-ferrites posses high saturation magnetization (Ms) which increases with the addition of Co^{2+} and high sintering temperature, very small coercivity, small retentivity with super-paramagnetic in nature at small doping of Co^{2+}. The saturation magnetization of the samples increases when the samples were calcined at higher temperature i.e. at 800 °C than at 600 °C. Saturation magnetization increases with the Co^{2+} substituion. Coercivity and the retentivity of the samples calcined at 800 °C also increases with the Co^{2+} substitution. The squareness ratio much smaller than 0.5 clearly indicated the uniaxial magnetocrystalline anisotropy of the samples and single domain (SD) nature of the nanoparticles. The magnetocrystalline anisotropy increases with the increase in the Co^{2+} content.

14.SUMMARY OF THE FINDINGS (IN 500 WORDS)

On next page

14.SUMMARY OF THE FINDINGS (IN 500 WORDS)

The prime aim of this research module was to develop the polycrystalline spinel superparamagnetic nano Ferro-spinels by sol- gel microwave assisted auto-combustion technique using urea as a fuel with particle size much smaller than 100 nm. Here we have doped transition metal Co^{2+} with +2 oxidation state in Nickel- Cadmium ferrites, so that Co^{2+} replaces some of the divalent cation from tetrahedral or octahedral lattice sites. The replacement has great impact on the structural, electrical and magnetic properties of the ferrites.

(a) Synthesis:

The based on proper stoichiometry, the weights of the oxidizers metal nitrates and organic fuels were calculated to prepare 30 gram samples of $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ with x = 0.0, 0.02, 0.05, 0.1, 0.2 and 0.3. The stoichiometric amounts of AR grade $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ $Fe(NO_3)_3{\cdot}9H_2O$, and $CO(NH_2)_2$ were dissolved in a 30 ml de-ionized water at room temperature The slurry solution was converted into a sol. The sol was then heated on a magnetic stirrer with a hot plate at a temperature of 70 °C to obtain a highly viscous gel. The gel was then transferred into a domestic microwave oven of 800Wso that spontaneous self combustion of the gel starts with a spark. The combustion process lasts till the complete fuel is exhausted. The burnt gel converts into voluminous and fluffy ash. The ash is ground to powder and then calcined at 800 °C in the air in a muffle furnace by increasing its temperature at a constant rate of 100 °C per hour. After calcinations the powders were again milled for 4 hours. The calcinations remove any un-reacted chemicals in the sample. It further helps to evolve the single phase of spinel ferrites.

(b) X-ray diffraction (XRD) study:

X-ray diffraction study was performed using MDI-Jade 5.0 software with PDF2 database of the samples. The presence of reflection planes (220), (311), (222), (400), (422), (511), and (440) with highest intensity peak at (311), a characteristic feature of cubic spinel ferrites confirmed the cubic inverse spinel ferrites with space group $Fd\bar{3}m$ (227). The samples calcined at 800 °C improved crystalline nature. The lattice parameter decreases with the substitution of Co^{2+} and also with high sintering temperature. The average crystallite size of the nano-particles

increases with the substitution of Co^{2+}. The structural parameters inter-planer spacing (d), Specific surface area, X-ray Density and Lattice strain were calculated.

(c) FEG-SEM and EDS study:

The morphology of the samples was studied by FEG-SEM analysis. SEM images showed the nano-ferrites particles more or less agglomerated. The crystallite size observed from the SEM method is larger than the calculated from XRD method. It indicates each nano-particle consist of many crystallites and supports the agglomeration of nano-particles. To confirm the elemental composition of the samples after synthesis, energy dispersive x-ray spectroscopic (EDAX) analysis was conducted for the representative samples with x = 0.0, 0.02 and 0.05. The results confirm the stoichiometric presence of each element without loss of elements or presence of impurity.

(d) FTIR study:

To validate the presence of tetrahedral and octahedral sites in the FTIR analysis of the samples were conducted. Results confirmed the two absorption frequency bands ν_1 and ν_2 that are the characteristic bands of the spinel ferrites corresponding to stretching vibration of metal cation (Me) – oxygen anion (O^{2-}) bond in tetrahedral and octahedral sites in all the samples. The force constants corresponding to octahedral and tetrahedral sites increases with the increment of Co^{2+}. The Debye temperature also found to increase with substitution of Co^{2+}.

(e) Magnetic Studies:

The magnetic characterization of the synthesized samples was conducted by VSM study at room temperature. The saturation magnetization (M_S), retentivity (Mr) and Coercivity (Hc) increases with the substitution of Co^{2+}. The coercivity of the samples decreases as the size of nanoparticles decreases which indicates that all the nanoparticles are single domain and have size smaller than multi-domain nanoparticles. The experimental and the observed magneton number of the samples were found to deviate and do not match which can be attributed to the spin disorder at the surface, spin canting and non-saturation due to arbitrary dispersed fine nanoparticles with high magneticrystalline anisotropy in the

samples. The disagreement in magnetic moment can be explained by calculatting spin canting angle based on the non-collinear arrangment of spin, considering three sub-lattice Yafet-Kittel (Y-K) model. The squareness ratio of the nanoparticles for samples calcined at 600 °C is 0.0692 - 0.0276 whereas for samples calcined at 800 °C it is 0.2252 - 0.0638. The squareness ratio much smaller than 0.5 clearly indicated the uniaxial magnetocrystalline anisotropy of the samples and single domain (SD) nature of the nanoparticles. The small coercivity and squareness ratio and non-saturation of the samples at even at high applied magnetic fields suggests that the most of the nanoparticles even if not all, are superparamagnetic in nature. The synthesized samples are of single domain grains leading to their usefulness in the magnetic recording for Hard Disk Device (HDD).

15.CONTRIBUTION TO THE SOCIETY
(GIVE DETAILS)

Superparamagnetic Ferro-spinel nanoparticles are used in medical diagnosis, targeted therapy of cancer, contrast enhancement agents for magnetic resonance imaging (MRI), Ferro-fluids which are colloidal liquids of magnetic nano-grains suspended in a fluid useful as liquid seals (for e.g. in HDDs), for efficient heat transfer (e.g. in loudspeakers), and in suspension systems. Magnetic hyperthermia is one of the most promising approaches to the cancer therapy. Due to their vast technological application they have been of great interest to researchers recently.

The Ferro-spinels we obtained are in the size range from 9-14 nm sufficietly smaller in size to render as single domain magnetic nanopaticles. Based on their characterizations and analysis of results, the properties of these nano-ferrites suggest they can be suitable candidates for potential applications in MLC, soft ferrites applications including biomedical application such as hyperthermia.

16.WHETHER ANY PH.D.ENROLLED/PRODUCED OUT OF THE PROJECT:

Yes

17.NO. OF PUBLICATIONS OUT OF THE PROJECT .....
(PLEASE ATTACH)

1. H.S. Ahamad, N.S. Meshram, S.B. Bankar, S.J. Dhoble, K.G. Rewatkar, Structural properties of $Cu_xNi_{1-x}Fe_2O_4$ nano ferrites prepared by urea-gel microwave auto combustion method, Ferroelectrics. 516 (2017) 67–73.

doi:10.1080/00150193.2017.1362285

2. Synthesis and study of Co doped Ni-Cd Ferro-spinels by Microwave Assisted Sol-Gel Auto-combustion Method.

   Article communicated to the journal "Ferroelectrics". The research ID for the same is 191125341.

3. Presented a paper on Synthesis and Study of Superparamagnetic Ferro-Spinels by Microwave Assisted sol-gel Auto-Combustion Method at International Conference on Multi-functional Advanced Materials ICMAM-2018 on 5-7th October, 2018, organised by Kamala Nehru Mahavidyalaya, Nagpur.

PRINCIPAL INVESTIGATOR)

(Halim Sagir Ahamad)

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