Development of Chemical Methodologies for Synthesis of α-Fe_2O_3 and $Ni_{1-x}Zn_xFe_2O_4$ ($0 < x < 1$) Nanopowders and Study of their Structural and Physical Properties

THESIS

Submitted in partial fulfilment
of the requirements for the degree of
DOCTOR OF PHILOSOPHY

by

PRITA PANT SARANGI

Under the Supervision of

Dr. Narendra Nath Ghosh

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN) INDIA
2010

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)

CERTIFICATE

This is to certify that the thesis entitled **"Development of Chemical Methodologies for Synthesis of α-Fe_2O_3 and $Ni_{1-x}Zn_xFe_2O_4$ (0 < x < 1) Nanopowders and Study of their Structural and Physical Properties"** which is submitted for award of Ph.D. Degree of the Institute, embodies original work done by her under my supervision.

Signature in full of the Supervisor:
Name in capital block letters: DR. NARENDRA NATH GHOSH
Designation: Assistant Professor

Date:

ACKNOWLEDGEMENT

I express my deep gratitude towards my guide, Dr. Narendra Nath Ghosh, for his able guidance, constant encouragement and tremendous support throughout the duration of my research work.

I am extremely grateful to Prof. K. E. Raman (Director, BITS Pilani, K. K. Birla Goa Campus) and to the higher authorities of BITS Pilani for providing me with the facilities to conduct my research work at BITS Pilani, K. K. Birla Goa Campus. I also express my gratitude towards late Prof. T. C. Goel (Former Director, BITS Pilani, K. K. Birla Goa Campus) whose motivation guided me to complete my research work.

I thankfully acknowledge financial support from DRDO (Project No. ERIP/ER/060/5042/M/01/929).

I am indebted to Dr. Rahul Mohan (NCAOR, Goa), Dr. V. S. Prasad (NIIST, Thiruvananthpuram), Dr. Rosilda Selvin (LUST, Taiwan) and Dr. S. R. Vadera (DRDO Lab, Jodhpur) for extending the experimental facilities in their lab.

I extend my sincere thanks to Dr. Sunil Bhand (Group Leader, Chemistry Group), Dr. A.P. Koley (Faculty-in-Charge, ARC & I), Dr. S. D. Manjare (Faculty-in-Charge, RCED Division) and Dr. R. N. Behra (Assistant Professor, Chemistry Group). Their help and support has been vital in the completion of this work.

I would also like to express my thanks to all my friends especially Mr. Bhanudas Naik, Mr. Amit Rajput, Dr. Arunashree Panda, Mrs. Kanchanmala Deshpande, Mrs. Princy Johnson, Mr. Digambar Waingankar and Mrs. Kamna Upadhyaya.

Finally, I am thankful to my family, especially to my husband, for their support and for the absolute faith they bestow on me.

ABSTRACT

Nanostructured α-Fe_2O_3 and series of Ni-Zn ferrite powders have gained immense importance in recent years due to their myriad potential applications in diverse fields. In this research work, three simple chemical methodologies have been successfully developed in order to synthesize single phase, nanostructured α-Fe_2O_3 and series of Ni-Zn ferrite powders. The average particle size of the synthesized nanoparticles lies in the range of ~ 15-50 nm. Nanoparticles of iron oxide are elongated while nanoparticles of Ni-Zn ferrite are round in shape. The synthesized nanopowders have high room temperature resistivity (10^5 -10^9 Ω cm) although the variation of resistivity with respect to temperature is affected by the presence of humidity in the atmosphere. However, the ferrite nanopowders sintered at 1200^0C, synthesized by all three chemical methodologies, exhibit the typical NTCR (negative temperature coefficient of resistance) behavior of ferrites. Room temperature magnetic measurements reveal that the synthesized Ni-Zn ferrite nanopowders possess saturation magnetization that varies between 30-60 emu/g depending on the method of preparation and the composition of the samples.

Advantages offered by these developed aqueous solution based chemical methods that make them attractive are:

(i) metal alkoxides or complex metal compounds, which are expensive, difficult to handle, synthesize, and sometimes toxic have not been used in the developed methods.

(ii) strong acid, base or organic solvents have not been used in any of the methods.

(iii) use of simple and cheap metal nitrates as starting materials and water as solvent helps in reducing the processing cost as compared to other reported wet chemical methods. Moreover, any elaborate experimental setup is not required for the synthesis of nanopowders by these methods.

(iv) Unlike other reported methods, Zn loss is not observed during high temperature sintering of pellets, prepared by the synthesized nanopowders. This ensures the maintenance of stoichiometry of the final product.

TABLE OF CONTENTS

	Page No.
Acknowledgement	(iii)
Abstract	(iv)
List of Figures	(ix)
List of Tables	(xiv)

1. Introduction

1.1 Scope of Research Work	1
1.2 Introduction to Iron Oxide (α-Fe_2O_3) and Ni-Zn Ferrites	1
1.3 Nanostructured Materials and their Processing	6
1.3.1 Solid State Method	7
1.3.2 Gas Phase Methods	7
1.3.3 Solution Phase Methods	8
1.4 Gap in Existing Research	11
1.5 Objective	12
1.6 Characterization Details	12
1.7 Outlay of the Thesis	14

2. Synthesis of α-Fe_2O_3 nanopowder by using PVA precursor based method

2.1 Experimental Procedure for Chemical Synthesis	15
2.2 Results and Discussion	15
2.2.1 Thermal Analysis	15
2.2.2 X-Ray Analysis	17
2.2.3 TEM Analysis	19
2.2.4 SEM Analysis	20
2.2.5 DC resistivity measurement	21

2.3 Summary of Results 23

3. **Synthesis of α-Fe_2O_3 nanopowder by using Oxalate precursor based method**

3.1 Experimental Procedure for Chemical Synthesis 25

3.2 Results and Discussion 25

3.2.1 Thermal Analysis 25

3.2.2 X-Ray Analysis 27

3.2.3 TEM Analysis 29

3.2.4 SEM Analysis 30

3.2.5 DC resistivity measurement 31

3.3 Summary of Results 33

4. Synthesis of α-Fe_2O_3 nanopowder by using EDTA precursor based method

4.1 Experimental Procedure for Chemical Synthesis 35

4.2 Results and Discussion 35

4.2.1 Thermal Analysis 35

4.2.2 X-Ray Analysis 37

4.2.3 TEM Analysis 39

4.2.4 SEM Analysis 40

4.2.5 DC resistivity measurement 41

4.3 Summary of Results 43

5. Synthesis of Ni-Zn ferrite nanopowders by using PVA precursor based method

5.1 Experimental Procedure for Chemical Synthesis 45

5.2 Results and Discussion 46

5.2 1 Thermal Analysis 46

5.2.2 X-Ray Analysis 50

5.2.3 TEM Analysis 52

5.2.4 SEM Analysis 54

5.2.5 DC resistivity measurement 55
5.2.6 Magnetization Measurement 59

5.3 Summary of Results 62

6. Synthesis of Ni-Zn ferrite nanopowders by using Oxalate precursor based method

6.1 Experimental Procedure for Chemical Synthesis 63
6.2 Results and Discussion 64
6.2.1 Thermal Analysis 64
6.2.2 X-Ray Analysis 67
6.2.3 TEM Analysis 69
6.2.4 SEM Analysis 71
6.2.5 DC resistivity measurement 72
6.2.6 Magnetization Measurement 76

6.3 Summary of Results 79

7. Synthesis of Ni-Zn ferrite nanopowders by using EDTA precursor based method

7.1 Experimental Procedure for Chemical Synthesis 80
7.2 Results and Discussion 81
7.2.1 Thermal Analysis 81
7.2.2 X-Ray Analysis 85
7.2.3 TEM Analysis 87
7.2.4 SEM Analysis 88
7.2.5 DC resistivity measurement 89
7.2.6 Magnetization Measurement 92
7.3 Summary of Results 95

8. Conclusions and Future Scope of Work

8.1 Comparative Summary of Results for the Three Developed Chemical Methodologies 96

8.2 Conclusions 98

8.3 Limitations of the developed chemical methods 99

Future Scope of Work 100

References 101-116

List of Publications **Appendix I**

Bio-data of Candidate **Appendix II**

Bio data of Supervisor **Appendix III**

List of Figures

Figure	Page No.
2.1 TG-DTG and DSC thermograms of the precursor in air. .	16
2.2 (a) X-ray diffraction spectra of precursor powder at different calcination temperatures (b) slow scan of the (104) and (110) diffraction planes.	18
2.3 TEM micrograph of α-Fe_2O_3 powder calcined at 450^0C.	19
2.4 SEM micrographs of α-Fe_2O_3 powder (a) calcined at 450^0C and (b) sintered at 1100^0C.	20
2.5 Variation of DC resistivity with change in temperature of α-Fe_2O_3 powder for (a) unsintered sample (b) sample sintered at 1100^0C.	22
3.1 TG-DTG and DSC thermograms of the precursor in air. .	26
3.2 (a) X-ray diffraction spectra of precursor powder at different calcination temperatures (b) slow scan of the (104) and (110) diffraction planes.	28
3.3 TEM micrograph of α-Fe_2O_3 powder calcined at 450^0C.	29
3.4 SEM micrographs of α-Fe_2O_3 powder (a) calcined at 450^0C and (b) sintered at 1100^0C.	30

3.5 Variation of DC resistivity with change in temperature of α-Fe_2O_3 powder for (a) unsintered sample (b) sample sintered at 1100^0C. 32

4.1 TG-DTG and DSC thermograms of the precursor in air. . 36

4.2 (a) X-ray diffraction spectra of precursor powder at different calcination temperatures (b) slow scan of the (104) and (110) diffraction planes. 38

4.3 TEM micrograph of α-Fe_2O_3 powder calcined at 450^0C. 39

4.4 SEM micrographs of α-Fe_2O_3 powder (a) calcined at 450^0C and (b) sintered at 1100^0C. 40

4.5 Variation of DC resistivity with change in temperature of α-Fe_2O_3 powder for (a) unsintered sample (b) sample sintered at 1100^0C. 42

5.1 TG-DTG and DSC thermograms of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ and (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ in air. 47-48

5.2 DSC thermograms of precursors powders for the series of $Ni_{1-x}Zn_xFe_2O_4$ ferrites. 49

5.3 XRD spectra of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ ferrites, at different calcination temperatures. Slow scan of the (311) diffraction plane are shown in the insets. Impurity phase is marked by (*) and corresponds to pure hematite. 50-51

5.4 TEM micrographs for the series of $Ni_{1-x}Zn_xFe_2O_4$ of nanopowders for (a) x = 0.35 and (b) x = 0.50, synthesized at a calcination temperature of 950^0C. 53

5.5 SEM micrographs of $Ni_{(1-x)}Zn_xFe_2O_4$ showing the change of microstructure with changing value of x and sintering condition (a) x= 0.2, unsintered, (b) x= 0.35, unsintered, (c) x= 0.5, unsintered, (d) x= 0.6, unsintered, (e) x= 0.2, sintered at 1100^0C, (f) x= 0.2, sintered at 1200^0C, (g) x= 0.2, sintered at 1200^0C, (h) x= 0.2, sintered at 1300^0C and (i) x= 0.6, sintered at 1300^0C. 54

5.6 DC resistivity for the series of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.20, 0.35, 0.50 and 0.60) nanopowders with respect to temperature for unsintered samples and samples sintered at 1100 and 1200^0C. Left Y axis is the scale for unsintered samples and samples sintered at 1100^0C. Right Y axis is the scale for samples sintered at 1200^0C. 56

5.7 Room temperature hysteresis loops for the series of $Ni_{1-x}Zn_xFe_2O_4$nanopowders. 60

6.1 TG-DTG and DSC thermograms of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ and (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ in air. 65-66

6.2 XRD spectra of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ ferrites, at different calcination temperatures. Slow scan of the (311) diffraction plane are shown in the insets. Impurity phase is marked by (*) and corresponds to pure hematite. 67-68

6.3 TEM micrographs for the series of $Ni_{1-x}Zn_xFe_2O_4$ of nanopowders for (a) x = 0.20 and (b) x = 0.60, synthesized at a calcination temperature of 850^0C. 70

6.4 SEM micrographs of $Ni_{(1-x)}Zn_xFe_2O_4$ showing the change of microstructure with changing value of x and sintering condition (a) x= 0.2, unsintered, (b) x= 0.35, unsintered, (c) x= 0.5, unsintered, (d) x= 0.6, unsintered, (e) x= 0.2, sintered at 1100^0C, (f) x= 0.2, sintered 71

at 1200^0C, (g) x= 0.2, sintered at 1200^0C, (h) x= 0.2, sintered at 1300^0C and (i) x= 0.6, sintered at 1300^0C.

6.5 DC resistivity for the series of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.20, 0.35, 0.50 and 0.60) nanopowders with respect to temperature for unsintered samples and samples sintered at 1100 and 1200^0C. Left Y axis is the scale for unsintered samples and samples sintered at 1100^0C and Right Y axis is the scale for samples sintered at 1200^0C for x = 0.20, 0.50 and 0.60 . For x = 0.35, scales are indicated in the figure. 73

.

6.6 Room temperature hysteresis loops for the series of $Ni_{1-x}Zn_xFe_2O_4$nanopowders. 76

7.1 TG-DTG and DSC thermograms of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ and (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ in air. 82-83

7.2 DSC thermograms of precursors powders for the series of $Ni_{1-x}Zn_xFe_2O_4$ ferrites. 84

7.3 XRD spectra of precursor powders of (a) $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (b) $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (c) $Ni_{0.50}Zn_{0.50}Fe_2O_4$ (d) $Ni_{0.40}Zn_{0.60}Fe_2O_4$ ferrites, at different calcination temperatures. Slow scan of the (311) diffraction plane are shown in the insets. 85-86

7.4 TEM micrographs for the series of $Ni_{1-x}Zn_xFe_2O_4$ of nanopowders for (a) x = 0.50 and (b) x = 0.60, synthesized at a calcination temperature of 450^0C. 87

7.5 SEM micrographs of $Ni_{(1-x)}Zn_xFe_2O_4$ showing the change of microstructure with changing value of x and sintering condition (a) x = 0.20, unsintered, (b) x = 0.35, unsintered, (c) x = 0.60, unsintered, (d) x = 0.35, sintered at 1100^0C, (e) x = 0.50, sintered at 1100^0C, (f) x = 0.20, sintered at 1200^0C, (g) x = 0.60, sintered at 1200^0C, (h) x = 0.20, sintered at 1300^0C, (i) x = 0.60, sintered at 1300^0C. 88

7.6 DC resistivity for the series of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.20, 0.35, 0.50 and 0.60) nanopowders with respect to temperature for unsintered samples and samples sintered at 1100 and 1200^0C. 90

7.7 Room temperature hysteresis loops for the series of $Ni_{1-x}Zn_xFe_2O_4$nanopowders. 93

List of Tables

Table	Page No.
1.1 Comparative room temperature DC resistivity of ferrites prepared by some representative methods.	4
1.2 Comparative room temperature magnetic parameters of Ni-Zn ferrite nanoparticles prepared by some representative methods.	5
5.1 Molar ratio of starting compounds.	45
5.2 Room temperature (25^0C) DC resistivity of Ni-Zn ferrites for unsintered samples and samples sintered at 1100 and 1200^0C.	57
5.3 Room temperature saturation magnetization and coercivity of different compositions.	59
6.1 Molar ratio of starting compounds.	63
6.2 Room temperature (27^0C) DC resistivity of Ni-Zn ferrites for unsintered samples and samples sintered at 1100 and 1200^0C.	74
6.3. Room temperature saturation magnetization and coercivity of different compositions.	76
7.1 Molar ratio of starting compounds.	80
7.2. Room temperature (25^0C) DC resistivity of Ni-Zn ferrites for unsintered samples and samples sintered at 1100 and 1200^0C.	91

7.3. Room temperature saturation magnetization and coercivity of different compositions. 94

8.1 Comparative summary of results for nanostructured α-Fe_2O_3 synthesized by PVA precursor based method (Method 1), Oxalate precursor based method (Method 2) and EDTA precursor based method (Method 3). 96

8.2 Comparative summary of results for nanostructured $Ni_{1-x}Zn_xFe_2O_4$ ($0 < x < 1$) synthesized by PVA precursor based method (Method 1), Oxalate precursor based method (Method 2) and EDTA precursor based method (Method 3). 97