EXPERIMENTAL INVESTIGATIONS OF IRON OXIDE BASED NANOSTRUCTURES AND THEIR CORRELATION WITH THEORY

In partial fulfillment of the requirements for the degree of
Doctor of Philosophy (Ph.D.)

In
Solid State Physics

By
Robina Ashraf
Roll. No. Ph.D.1101
Session 2011-2016

Centre of Excellence in Solid State Physics
University of the Punjab
Quaid–e–Azam Campus, Lahore
Abstract

The present study deals with synthesis of different iron oxide (magnetite, maghemite and hematite) based nanostructures using sol-gel method. The main emphasis is to experimentally synthesize iron oxide based nanostructures and to correlate these results with theory.

Molarity, pH, temperature and surfactant of the sol are important parameters to control morphology. Hence, in this research work all of the 4 parameters were optimized to study their effect on structural, morphological, optical and magnetic properties. In the first step seven different sols with varying concentrations from 1.8 to 0.6 mM are synthesized. The concentration of 1.4 mM results in a pure magnetite phase whereas others show mixed magnetite and maghemite phases. Free growth of iron oxide nanostructures, including nanoneedles, nanorods, nanospheres and nanobrushes, are observed in scanning electron microscope images.

In the second step 1.4mM sol concentration is used and nine sols are synthesized with pH 1 to 9. Samples exhibit magnetite phase with superparamagnetic nature at low pH (1, 2 & 6) with 50nm diameter nanoparticles. For pH 3-5 hematite phase is observed while with further increase in pH (7&8) maghemite phase is achieved. Annealing for pH 1-8 only strengthened the existing phases rather than transformation. Maghemite and hematite phases are observed at pH 9 with annealing at 200 °C and 300 °C respectively.

In the third step effect of surfactants was studied in detail. PVA, triton X-100 and oleic acid are used as surfactants. Sols thus prepared are analyzed magnetically before and after room temperature aging. Superparamagnetic behaviour is observed for iron oxide sol synthesized using oleic acid as surfactant, and therefore was selected for further studies. The amount of oleic acid is varied as 5%, 10% and 15% by volume. Shape and morphology of iron oxide nanoparticles strongly depend on calcination temperature, which is varied from 300°C to 900°C. Iron oxide sol with 15% by volume show superparamagnetic behavior while sols prepared with 5% and 10% oleic acid show dia-ferromagnetic and para-ferromagnetic mixed behavior. Two types of NPs are observed in SEM images; one with shell and one without shell with 10% oleic acid. Cubic NPs with size less than 25nm and highest dielectric constant of ~107.5 (log f = 5.0) is observed with 15% oleic acid at 500°C.

ZnO is selected for iron oxide based nanostructures. Once again sol-gel method has been employed for synthesis of iron oxide added ZnO nanoparticles. The dopant concentration is varied as 1wt% to 5wt%. Ferromagnetic behavior of Fe added ZnO nanoparticles arise due to the presence of long range oscillating interactions among the free charge carriers. The band gap of these iron oxide based nanostructures is in the range of 3.05eV to 3.48eV.
Mn/Fe co-doped ZnO structures are also prepared by simple sol-gel and spin coating method. Five different sols with the change in concentration (1-5wt%) of both Mn and Fe are synthesized. Molar ratio of Mn and Fe is kept constant, i.e., 1:1. Sols are spun onto glass and copper substrates by spin coating method followed by the post magnetic field annealing at 300 °C for 1 h. XRD results show incorporation of Mn and Fe in the host lattice up to a dopant concentration of 4wt%. Small crystallites of Mn and Fe$_2$O$_3$ are observed by increasing the dopant concentration to 5wt%. VSM results indicate room temperature ferromagnetism in all samples. Moreover, Mn/Fe co-doped thin films show magnetic hysteresis equivalent to that of multilayered structure, indicating that such complex structures can be replaced by a single ZnO layer with co-doping of Mn and Fe.

Density functional theory is used for the theoretical investigation of iron oxide based nanostructures. Amsterdam Density Functional (ADF) software with BAND tool is used. Generalized Gradient Approximation (GGA) and Local Density Approximation (LDA) are used in order to correlate structural, optical and magnetic properties of iron oxide based nanostructures. With basis set of TZ2P geometry optimization is achieved. Underestimation of electronic properties of all phases is observed by GGA and LDA. While, improved value of band gap is obtained by GGA+U and LDA+U. Exchange correlational potential is also optimized in case of GGA+U calculations. Hubbard potential (U eV) is optimized and lowest value of U i.e. 0.6 eV is used for all calculations for wüstite, hematite, maghemite and magnetite. Total DOS and partial density of states for iron and oxygen are also studied for both approximations. Analysis of the density of states confirms the strong hybridization between Fe 3d and O 2p states in iron oxide. In all cases (magnetite, maghemite and hematite) density of states plots confirm that the main reason for the magnetic properties in iron oxide based nanostructures is the d orbital electrons. As a result, a good correlation of theory with experiment is being reported in this thesis.
Acknowledgements

With the name of Almighty ALLAH, the most Merciful and the most Beneficent, Who created the universe with ideas of beauty, symmetry and harmony and give us the abilities to discover that He thought but without His will nothing can be aspired and achieved. It is with great submission that I bow my head before Him for giving me the courage and fortitude to complete this work. I offer my humblest words of thanks to my Master Hazrat Muhammad (S.A.W), who is the true Prophet of ALLAH, Who is forever a torch of guidance and knowledge for humanity.

Ph.D. would not have been possible without the support of others; so many people have contributed their time and efforts to support me for accomplishing this work. First and foremost I would like to express my sincere gratitude to my kind supervisor Dr. Saira Riaz. She has taught me invaluable skills as a scientific researcher and critic, especially the ability to approach scientific questions with a solid understanding of solid state physics. Again, I express my most sincere gratitude to Dr. Saira Riaz for her support in my development as a scholarly researcher.

I would like to express my gratitude to my supervisor Prof. Dr. Shahzad Naseem for the continuous support of my PhD study and research, for his motivation and guidance he showed me until the successful end of my thesis. Also being Director, Centre of Excellence in Solid State Physics; Prof. Dr. Shahzad Naseem, has very kindhearted personality and has most cooperative behavior. He feels delight in struggling for the welfare of the students.

I am thankful to Dr. Tariq Mahmood (Assistant Professor, Government College Women University, Sialkot) for his guidance in theoretical research work. I am also thankful to all teachers in my life especially those who taught me at the COE in Solid State Physics.

Help of Prof. Guo Yan-Jun of Nanocentre at Chinese Academy of Sciences in providing me facilities for Raman characterization is highly acknowledged.
Lastly, but always first in my heart, thank you to my family specially my Father (Prof. Dr. Muhammad Ashraf), Mother (Ms. Haleema Bibi), Sisters and Brothers (Specially Naveed Ashraf) and Friends for listening to my excited explanations of what I am actually doing and supporting me in all my academic endeavors in countless ways, both large and small.

Finally, I would like to thank my Dear Husband (Dr. Muhammad Hassan Siddiqi) for his understanding and belief in me and in my work. Support and prayers from my In Laws (specially my respectable Father in law, Mian Allah Bukhsh) make it really possible otherwise it would have been impossible for me to successfully complete my Ph.D. It gives me an immense pleasure to acknowledge my sincere thanks to the people who have helped me directly or indirectly for making this research work possible.

(Robina Ashraf)
Abbreviations

ADF   Amsterdam density Function
BAND  Amsterdam Density Functional Band-Structure Program
CAPZ  Ceperley–Alder–Perdew–Zunger
DFT   Density functional theory
DFTB  Temperature Dependent Density Functional Program
DOS   Density of states
$E_0$  Ground state energy
GGA   Generalized gradient approximation
HF    Hartree Fock
IONPs Iron oxide Nanoparticles
LDA   Local density approximation
MM    Molecular Mechanics
PBE   Perdew–Burke–Ernzerhof
QMMM  Quantum Mechanics / Molecular Mechanics
Quild Quantum-regions Interconnected by Local Descriptions
ReaxFF Reax Force Field
TF    Thin films
TZ2P  Triple zeta with 2 polarization functions
UFF   Universal Force Field
VXC   Exchange correlation potential
$Z_a$  Nuclear charges
$\rho(r)$  Electronic density
It is certified that research work contained in the thesis has been performed by Ms. Robina Ashraf Roll No. Ph.D.1101, Session (2011-2016), as a partial fulfill requirement for the award of degree of Doctor of Philosophy in Solid State Physics and she allowed submitting it, to Centre for Excellence in Solid State Physics, University of the Punjab, Lahore.

Research Supervisor

Dr. Saira Riaz,
Associate Professor
Centre of Excellence in Solid State Physics,
University of the Punjab, Lahore.

Research Supervisor

Prof. Dr. Shahzad Naseem,
Director
Centre of Excellence in Solid State Physics,
University of the Punjab, Lahore.

Director

Prof. Dr. Shahzad Naseem,
Director
Centre of Excellence in Solid State Physics
University of the Punjab, Lahore.
Dedication

This work is dedicated to my Parents who have been the source of inspiration since my childhood and who were always there to help me, gave me courage and strength to accomplish all the goals of my life including this prestigious research achievement also to

Ms. Quratul-Ain (May Allah grant her High rank in Jannah) Whose unbelievable death was unbearable lose in my life.
Author Declaration

I Robina Ashraf hereby stated that my PhD thesis titled “Experimental Investigations of Iron Oxide Based Nanostructures and their Correlation with Theory” is my own work and has not been submitted previously by me for taking any degree from this University of the Punjab, Quaid-i-Azam Campus, Lahore or anywhere else in the country/world.

At any time if my statement is found to be incorrect even after my graduate the university has the right to withdraw my PhD degree.

(Robina Ashraf)

13-09-2017
# Table of Contents

Abstract .......................... ii  
Acknowledgements .................. iv  
Abbreviations ...................... vi  
Certificate ........................ vii  
Dedication ........................ viii  
Author Declaration ................. ix  
Table of Contents .................. x  
List of Tables ..................... xv  
List of Figures .................... xvii  

## CHAPTER-1  

1. Introduction .......................... 2  
1.1 Introduction .......................... 2  
1.2 Goals and Applications of Nanotechnology ........... 2  
1.3 Nanostructures ..................... 3  
1.3.1 Classification of Nanostructures ................. 3  
1.4 Nanoparticles ..................... 4  
1.4.1 Potential Applications of Nanoparticles .......... 4  
1.5 Iron Oxide ......................... 5  
1.5.1 Iron Oxide Phases ................. 5  
1.5.1.1 Wüstite (FeO) .................. 7  
1.5.1.2 Hematite (α-Fe₂O₃) .......... 7  
1.5.1.3 Maghemite (γ-Fe₂O₃) .......... 8  
1.5.1.4 Magnetite (Fe₃O₄) .......... 9  
1.5.2 Iron Oxide Nanostructures .......... 10  
1.6 Iron Oxide Based Zinc Oxide ............... 11  
1.6.1 Physical Properties ............... 11  
1.6.2 Chemical Properties ............. 12  
1.6.3 Mechanical Properties .......... 12  
1.6.4 Electrical Properties .......... 13  
1.6.5 Optical Properties ............. 13  
1.6.6 Magnetic Properties .......... 13  
1.6.7 Crystal Structure ............... 13  
1.6.7.1 Wurtzite Structure of Zinc oxide .......... 14  
1.6.7.2 Zinc Blende Structure of Zinc oxide .......... 14  
1.6.7.3 Rock Salt Structure of Zinc oxide .......... 15  
1.6.8 Zinc oxide Nanostructures .......... 15  
1.7 Goals and Objective ............... 15  
1.8 Layout of the Thesis ............... 16
CHAPTER-2

2.1 INTRODUCTION

2.2 AMSTERDAM DENSITY FUNCTIONAL (ADF)
   2.2.1 Background and History of ADF
   2.2.3 Basic Programs in ADF
   2.2.4 Measuring Properties/Calculations by ADF
   2.2.5 Applicability

2.3 BAND
   2.3.1 Functionality and Applicability
   2.3.2 Formalism
   2.3.3 Starting up with sub Program DIRAC
   2.3.4 Basis and Basis Sets
   2.3.5 Frozen Core Approximations
   2.3.6 Poisson’s Equation

2.4 DENSITY FUNCTIONAL THEORY (DFT)
   2.4.1 Motivation for DFT with Solution of Schrödinger Equation
   2.4.2 Neglecting the Solution of the Schrödinger Equation
   2.4.3 The Hohenburg-Kohn Theorems

2.5 THE ENERGY FUNCTIONAL
   2.5.1 Local Density Approximation (LDA)
      2.5.1.1 Disadvantages of Local Density Approximation
   2.5.2 Generalized Gradient Approximation (GGA)
   2.5.3 Meta-GGA Functional
   2.5.4 Hybrid Exchange Functional

2.6 SUMMARY

CHAPTER-3

3.1 INTRODUCTION

3.2 EXPERIMENTAL INVESTIGATIONS OF IRON OXIDE NANOSTRUCTURES

3.3 THEORETICAL INVESTIGATIONS OF IRON OXIDE NANOSTRUCTURES

3.4 INVESTIGATIONS ON IRON OXIDE BASED NANOSTRUCTURES

3.5 SUMMARY

CHAPTER-4

4.1 INTRODUCTION

4.2 SYNTHESIS APPROACHES
   4.2.1 Top-Down Approach
   4.2.2 Bottom-Up Approach
4.3 SOL-GEL TECHNIQUE
   4.3.1 Advantages of Sol-Gel Process
4.4 CHARACTERIZATION
   4.4.1 X-Ray Diffractometer (XRD)
     4.4.1.1 Bruker D8 Advance Diffractometer
   4.4.2 Scanning Electron Microscope (SEM)
     4.4.2.1 Hitachi S-3400N SEM
   4.4.3 Vibrating Sample Magnetometer (VSM)
     4.4.3.1 Lakeshore 7407 VSM
   4.4.4 Impedance Analyzer
     4.4.4.1 Analysis using Impedance Analyzer
     4.4.4.2 6500B Impedance Analyzer
   4.4.5. Raman Spectroscopy
     4.4.5.1 Basic Principle of Raman Spectroscopy
     4.4.5.2 Working and Operation of Raman Spectroscopy
     4.4.5.3 Renishaw inVia Raman Spectroscope
   4.4.6 Fourier Transform Infrared Spectroscopy
   4.4.7 Spectroscopic Ellipsometry
     4.4.7.1 Instrumentation of Ellipsometer
     4.4.7.2 Calculations
     4.4.7.4 J.A. Woollam Ellipsometer

CHAPTER-5

CHAPTER – 5  EFFECTS OF VARIATION IN SOL CONCENTRATION
   5.1 INTRODUCTION
   5.2 IRON OXIDE NANOSTRUCTURES WITH VARIATION IN SOL CONCENTRATION
   5.3 EXPERIMENTAL DETAILS
   5.4 RESULTS AND DISCUSSION
   5.5 SUMMARY

CHAPTER-6

CHAPTER – 6  EFFECTS OF VARIATION IN pH
   6.1 INTRODUCTION
   6.2 EXPERIMENTAL DETAILS
     6.2.1 Materials
     6.2.2 Magnetic Nanoparticle Synthesis
     6.2.3 Characterization
   6.3 RESULTS AND DISCUSSION
     6.3.1 Structural Properties
     6.3.2 Morphological Properties
     6.3.3 Raman Analysis
     6.3.4 Optical Band Gap
List of Tables

TABLE 1.1: DETAIL OF DIFFERENT PHASES OF IRON OXIDE WITH THEIR PROPERTIES ....................6
TABLE 1.2: PHYSICAL PROPERTIES OF BULK ZnO .....................................................................12
TABLE 6.1A. LATTICE PARAMETERS OF IRON OXIDE NANO PARTICLES SYNTHESIZED AT DIFFERENT pH ......................................................................................................................81
TABLE 6.1B. LATTICE PARAMETERS OF IRON OXIDE NANO PARTICLES SYNTHESIZED AT DIFFERENT pH .................................................................................................................................82
TABLE 6.1C. UNIT CELL VOLUME OF IRON OXIDE NANO PARTICLES SYNTHESIZED AT DIFFERENT pH ..............................................................................................................................................82
TABLE 6.1D. UNIT CELL VOLUME OF IRON OXIDE NANO PARTICLES SYNTHESIZED AT DIFFERENT pH (5-9) ..............................................................................................................................................83
TABLE 7.1: COMPARISON OF STRUCTURAL AND MAGNETIC PROPERTIES OF IRON OXIDE NPs .....113
TABLE 7.2: ZVIEW FITTING PARAMETERS FOR IRON OXIDE NANO PARTICLES SYNTHESIZED WITH SOL-C ......................................................................................................................................................117
TABLE 8.1: STRUCTURAL PROPERTIES OF IRON DOPED ZnO NPs .............................................125
TABLE 8.2: COMPARISON OF MAGNETIC PROPERTIES OF IRON DOPED ZnO NPs WITH LITERATURE ...............................................................................................................................................129
TABLE 9.1: COMPARISON OF SATURATION MAGNETIZATION OF UN-DOPED, DOPED AND CO-DOPED ZnO NANOSTRUCTURE BASED THIN FILMS ........................................................................................................138
TABLE 10.1: ATOMIC POSITIONAL PARAMETERS FOR WÜSTITE ....................................................142
TABLE 10.2: COMPARISON OF BAND GAP VALUES BY USING GGA, GGA+U, LDA AND LDA+U (U=0.6 eV) ......................................................................................................................................................150
TABLE 11.1: ATOMIC POSITIONAL PARAMETERS FOR HEMATITE ................................................155
TABLE 12.1: ATOMIC POSITIONAL PARAMETERS FOR MAGHEMITE ............................................163
TABLE 13.1: ATOMIC POSITIONAL PARAMETERS FOR MAGNETITE ................................................173
List of Figures

Figure 1.1: Crystal structure of wüstite (Yu and Zhou 2017) ........................................... 7
Figure 1.2: Crystal structure of hematite (Yu and Zhou 2017) ........................................... 8
Figure 1.3: Crystal structure of maghemite (Wu et al. 2015) ............................................ 9
Figure 1.4: Crystal structure of magnetite (Yu and Zhou 2017) ........................................ 10
Figure 1.5: Wurtzite structure of zinc oxide (Espitia et al. 2012) ...................................... 14
Figure 1.6: Cubic crystal structure for zinc blend (Espitia et al. 2012) .............................. 14
Figure 1.7: Rock salt structure (Espitia et al. 2012) .......................................................... 15
Figure 4.1: Flow diagram of sol-gel process (Righini and Chiappini 2014) ....................... 54
Figure 4.2: Bruker D8 Advanced X-ray Diffractometer .................................................... 56
Figure 4.3: Signals produced by SEM (Scrivener 1989) .................................................... 56
Figure 4.4: Hitachi S-3400N Scanning electron microscope ........................................... 57
Figure 4.5: Lakeshore 7407 VSM ................................................................................ 58
Figure 4.6: 6500B Impedance Analyzer ............................................................................ 59
Figure 4.7: Working of Raman spectroscopy ................................................................... 61
Figure 4.8: Renishaw InVia Raman Spectroscope ............................................................. 61
Figure 4.9: Main parts of Ellipsometer ............................................................................. 62
Figure 4.10: Incident reflected and transmitted light .......................................................... 63
Figure 4.11: J. A. Woollam M-2000 Ellipsomete ............................................................... 64
Figure 5.1: XRD patterns of films deposited using sol concentration of (a) 1.8, (b) 1.6,
(c) 1.4, (d) 1.2, (e) 1, (f) 0.8, and (g) 0.6 mM: i) As-deposited, ii) 60 min, and iii) 120 min
annealed at 300 °C (*Fe3O4; γ-Fe2O3). ........................................................................... 68
Figure 5.2: (A) Crystallite size & crystallinity and (B) texture coefficient of magnetic
field annealed iron oxide for 120 min ........................................................................... 69
Figure 5.3: SEM images of iron oxide nanostructures deposited with sol
concentration. (a) 1.8 mM, (b) 1.6 mM, (c) 1.4 mM, (d) 1.2 mM, (e) 1 mM, (f) 0.8 mM. .71
Figure 5.4: M–H curves of iron oxide nanostructures ....................................................... 71
Figure 5.5: (A) Saturation magnetization & coercivity and (B) MB/F.U. as a function of
sol concentration ....................................................................................................... 72
Figure 6.1: Schematic approach for iron oxide nanoparticles ......................................... 76
Figure 6.2: XRD patterns for iron oxide nanoparticles synthesized at pH 1 ................. 77
Figure 6.3: XRD patterns for iron oxide nanoparticles synthesized at pH 2 .................... 77
Figure 6.4: XRD patterns for iron oxide nanoparticles synthesized at pH 3 ................. 78
FIGURE 6.5: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 4. .................78
FIGURE 6.6: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 5. .................78
FIGURE 6.7: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 6. .................79
FIGURE 6.8: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 7. .................79
FIGURE 6.9: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 8. .................80
FIGURE 6.10: XRD PATTERNS FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 9. .................80
FIGURE 6.11: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 1. ........84
FIGURE 6.12: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 2. ........84
FIGURE 6.13: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 3. ........84
FIGURE 6.14: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 4. ........85
FIGURE 6.15: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 5. ........85
FIGURE 6.16: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 6. ........85
FIGURE 6.17: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 7. ........86
FIGURE 6.18: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 8. ........86
FIGURE 6.19: CRYSTALLITE SIZE FOR IRON OXIDE NANOPARTICLES SYNTHESIZED AT pH 9. ........86
FIGURE 6.20: SEM MICROGRAPHS OF IRON OXIDE NANOPARTICLES WITH VARIATION IN pH 1, 3, 6, 7 & 9 IN A – E RESPECTIVELY .................................................................87
FIGURE 6.21: RAMAN ANALYSIS OF IRON OXIDE NANOPARTICLES WITH pH VARIATION ..........89
90
FIGURE 6.22: VARIATION OF BAND GAP FOR pH 1-9. .................................................................90
FIGURE 6.23: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 1 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................91
FIGURE 6.24: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 2 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................91
FIGURE 6.25: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 3 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................92
92
FIGURE 6.26: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 4 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................92
92
FIGURE 6.27: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 5 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................92
FIGURE 6.28: M-H CURVES FOR IRON OXIDE NANOPARTICLES SYNTHESIZED WITH pH 5 AND (A) ANNEALED AT 200˚C AND 300˚C; (B) MF ANNEALED AT 200˚C AND 300˚C......................93
Figure 6.29: M-H curves for iron oxide nanoparticles synthesized with pH 7 and (A) annealed at 200°C and 300°C; (B) MF annealed at 200°C and 300°C. .......................... 93

Figure 6.30: M-H curves for iron oxide nanoparticles synthesized with pH 8 and (A) annealed at 200°C and 300°C; (B) MF annealed at 200°C and 300°C. .......................... 93

Figure 6.31: M-H curves for iron oxide nanoparticles synthesized with pH 9 and (A) annealed at 200°C and 300°C; (B) MF annealed at 200°C and 300°C. .......................... 94

Fig. 6.32: Saturation magnetization for iron oxide nanoparticles synthesized with pH 1. .................................................................................................................. 94

Figure 6.33: Saturation magnetization for iron oxide nanoparticles synthesized with pH 2. .................................................................................................................. 95

Figure 6.34: Saturation magnetization for iron oxide nanoparticles synthesized with pH 3. .................................................................................................................. 95

Figure 6.35: Saturation magnetization for iron oxide nanoparticles synthesized with pH 4. .................................................................................................................. 95

Figure 6.36: Saturation magnetization for iron oxide nanoparticles synthesized with pH 5. .................................................................................................................. 96

Figure 6.37: Saturation magnetization for iron oxide nanoparticles synthesized with pH 6. .................................................................................................................. 96

Figure 6.38: Saturation magnetization for iron oxide nanoparticles synthesized with pH 7. .................................................................................................................. 96

Figure 6.39: Saturation magnetization for iron oxide nanoparticles synthesized with pH 8. .................................................................................................................. 97

Figure 6.40: Saturation magnetization for iron oxide nanoparticles synthesized with pH 9. .................................................................................................................. 97

Figure 7.1: Bonding of oleic acid with iron oxide nanoparticles. .............................................................. 102

Figure 7.2: Magnetic hysteresis curves for iron oxide sols obtained at room temperature a) Sol A, b) Sol B, c) Sol C, d) Sol D, e) Sol E, f) Sol F and g) Sol G. 104

Figure 7.3: XRD patterns of iron oxide nanoparticles synthesized by Sol E with PVA as surfactant. .................................................................................................................. 105

Figure 7.4: XRD patterns of iron oxide nanoparticles synthesized by Sol-G with Triton X-100 as surfactant. ........................................................................................................ 105

Figure 7.5: XRD patterns of a) iron oxide nanoparticles synthesized by Sol B, b) iron oxide nanoparticles synthesized by Sol-C. ........................................................................ 106
**Figure 7.6:** (A) Lattice constants; (B) Unit cell volume of iron oxide nanoparticles calculated with increasing calcination temperature. ........................................ 107

**Figure 7.7:** (A) Variation in crystallite size with calcination temperature (B) Variation in specific surface area with calcination temperature. ......................... 108

**Figure 7.8:** SEM image of iron oxide nanoparticles prepared with Sol A. ...................... 108

**Figure 7.9:** SEM image of iron oxide nanoparticles prepared using Sol-B and calcined at (A) 300°C (B) 500°C and (C) 700°C. ................................................. 109

**Figure 7.10:** SEM images of iron oxide nanoparticles synthesized using Sol-C at calcination temperature of (A) 300°C (B) 500°C (C) 700°C and (D) 900°C............. 110

**Figure 7.11:** Room temperature M-H curves prepared using (A) Sol-A (B) Sol-B and (C) Sol-C. ........................................................................................................ 112

**Figure 7.12:** Comparison of saturation magnetization of nanoparticles prepared using Sol-A, Sol-B and Sol-C ........................................................................... 112

**Figure 7.13:** (A) Dielectric constant (B) Tangent loss for iron oxide nanoparticles synthesized using Sol-A. ................................................................. 114

**Figure 7.14:** (A) Dielectric constant (B) Tangent loss for iron oxide nanoparticles synthesized using Sol-B. ................................................................. 114

**Figure 7.15:** (A) Dielectric constant (B) Tangent loss for iron oxide nanoparticles synthesized using Sol-C. ................................................................. 115

**Figure 7.16:** (A) Dielectric constant (B) Tangent loss for iron oxide nanoparticles plotted as a function of calcination temperature at log f = 5.0............. 116

**Figure 7.17:** Cole-Cole plot for iron oxide nanoparticles prepared with Sol-C .... 116

**Figure 8.1:** Fe doped ZnO sols with 0-5 wt% Fe doping........................................ 122

**Figure 8.2:** Fe doped ZnO sols and nanoparticles with 0-5 wt% Fe doping ............ 122

**Figure 8.3:** XRD patterns for iron doped ZnO NPs ............................................ 123

**Figure 8.4:** Crystallite size for iron doped ZnO NPs plotted as function of dopant concentration ..................................................................................................... 124

**Figure 8.5:** FTIR spectra of iron doped ZnO NPs ................................................. 125

**Figure 8.6:** Transmission curves for iron doped ZnO NPs .................................... 126

**Figure 8.7:** (A) $A^2$ vs. E(eV) plots (B) Band gap as a function of dopant concentration for iron doped ZnO NPs ................................................................. 127

**Figure 8.8:** M-H curves for iron doped ZnO NPs ............................................. 128

**Figure 8.9:** Saturation magnetization and coercivity as a function of dopant concentration ..................................................................................................... 128
Figure 9.1: XRD pattern of Mn doped ZnO .................................................................133

Figure 9.2: XRD graphs of (A) un-doped, (B) 4wt% and (C) 5wt% Mn/Fe co-doped ZnO
nanostructures based thin films (*Mn/Fe2O3). ..........................................................133

Figure 9.3: SEM micrographs of the Mn/Fe co-doped ZnO nanostructured thin films
with (A) 1wt%, (B) 2wt%, (C) 3wt%, (D) 4wt%, and (E) 5wt%. ...............................135

Figure 9.4: Hysteresis loop of 5wt% Mn doped ZnO. Inset: Hysteresis loop of 1-5wt%
Mn doped ZnO. ...........................................................................................................136

Figure 9.5: Hysteresis loops of Mn/Fe co-doped ZnO nanostructured thin films at
various doping concentration. Inset: Hysteresis loop indicates presence of
multilayered like structure formed by co-doping of Mn and Fe ions in ZnO for
3wt% Mn/Fe co-doping. ..............................................................................................136

Figure 9.6: Saturation magnetization and squareness versus dopant concentration.
........................................................................................................................................137

Figure 10.1: Formation energy versus unit cell volume curve for wüstite. ...............143

Figure 10.2: Structure of wüstite at 0K (Red atoms of iron and blue ones are of
Oxygen atoms) ..............................................................................................................144

Figure 10.3: Band structure of wüstite calculated by LDA a) Combine spin-up and spin-
down, b) for spin-up state and c) for spin-down state. .................................................145

Figure 10.4: Band structure of wüstite calculated by GGA a) Combine spin-up and
spin-down, b) for spin-up state and c) for spin-down state. .........................................146

Figure 10.5: a) Partial and b) total DOS by LDA ..........................................................146

Figure 10.6: a) Partial and b) total DOS by GGA..........................................................147

Figure 10.7: Variation of the band gap with the applied Hubbard potential using the
LDA and GGA. ..............................................................................................................148

Figure 10.8: Band structure of wüstite calculated by LDA+U; a) Combine spin-up and
spin-down, b) for spin-up state and c) for spin-down state. .........................................149

Figure 10.9: Band structure of wüstite calculated by GGA+U; a) Combine spin-up and
spin-down, b) for spin-up state and c) for spin-down state. .........................................150

Figure 10.10: a) Partial and b) total DOS by LDA+U ................................................151

Figure 10.11: a) Partial and b) total DOS by GGA+U..................................................152

Figure 11.1: Formation energy versus unit cell volume curve for hematite..............156

Figure 11.2: Crystal structure of hematite a) supercell and b) unit cell after
gelometry optimization by ADF. Color scheme O=red atoms and Fe=dark gray. .157
Figure 11.3: a) Band structure of hematite b) Band structure for spin-up states and c) band structure for spin-down states, calculated by GGA ........................................ 158

Figure 11.4: a) Partial DOS b) Total density of states of hematite calculated by GGA. ..................................................................................................................................................... 158

Figure 11.5: Variation of Hubbard potential for Generalized Gradient Approximation ......................................................................................................................... 159

Figure 11.6: a) Band structure of hematite b) Band structure for spin-up states (inset: direct band gap) and c) Band structure for spin-down states, calculated by GGA+U. ...................................................................................................................... 160

Figure 11.7: a) Partial (all states of oxygen and iron) DOS; b) Total DOS of hematite by using GGA+U. ........................................................................................................................................... 160

Figure 12.1: Formation energy verses unit cell volume curve for maghemite. .......... 164

Figure 12.2: Structure of super cell of maghemite. ........................................................ 165

Figure 12.3: a) Band structure of maghemite b) Band structure for spin-up states and c) band structure for spin-down states, calculated by GGA ......................................................... 166

Figure 12.4: a) Partial (all states of oxygen and iron) DOS; b) Total DOS of maghemite by using GGA. ........................................................................................................................................ 167

Figure 12.5: a) Band structure of maghemite b) Band structure for spin-up states and c) band structure for spin-down states, calculated by GGA+U. .................................................... 168

Figure 12.6: a) Partial DOS; b) Total DOS of maghemite by using GGA+U. .......... 169

Figure 13.1 Formation energy verses unit cell volume curve of magnetite. .......... 174

Figure 13.2 a) Crystal structure of super cell of magnetite; b) Unit cell. Color scheme Blue= oxygen, yellow= iron. ........................................................................................................ 174

Figure 13.3: a) Band structure of magnetite b) Band structure for spin-up states and c) band structure for spin-down states, calculated by GGA. ......................................................... 175

Figure 13.4: a) Partial (all states of oxygen and iron) DOS; b) Total DOS of magnetite by using GGA. ........................................................................................................................................ 176

Figure 13.5: a) Band structure of magnetite b) Band structure for spin-up states and c) band structure for spin-down states, calculated by GGA+U. .................................................... 177

From Figure 13.5 (a) band gap of 0.89 eV is observed which is also confirmed from total density of states of magnetite [Figure 13.6 (b)] obtained after applying Hubbard potential of 0.6 eV. Charge transfer from 2p states of oxygen to 3d states of iron is observed from Figure 13.6 (a). ........................................................................................................ 177
FIGURE 13.6: a) Partial (all states of oxygen and iron) DOS; b) Total DOS of magnetite by using GGA+U. .......................................................... 177

FIGURE 14.1: a) Supercell of iron doped ZnO and b) supercell of Mn/Fe co-doped ZnO (Golden atoms=Fe, Silver=Zn, Red=O and Green=Mn). .................................................. 181

FIGURE 14.2: Band structure of Fe doped ZnO calculated by GGA+U. ......................... 181

FIGURE 14.3: Band structure of Mn/Fe co-doped ZnO calculated by GGA+U. ............. 182

FIGURE 14.4: Density of states of Fe doped ZnO calculated by GGA+U. ..................... 182

FIGURE 14.5: Density of states of Mn/Fe co-doped ZnO calculated by GGA+U. .......... 182
Chapter – 1

1.1 Introduction

Nanotechnology has been fascinating consideration since the last 2 decades or so because it offers many exciting advantages (King et al. 2017). The development of this multidisciplinary technology motivates the researchers in the field of material science, physics and biotechnology. These efforts lead to the search of new theory and phenomenon for industrial revolutions as well. Nanotechnology produces lighter, faster, smaller and economic devices and hence became the most popular field due to development in technology (Roco and Bainbridge 2005). In 1959, Richard Feynman gave new horizons by delivering his revolutionary lecture, “There is Plenty of Room at the Bottom” (Feynman 1960). This leads in promptly increasing trend of technology at nanoscale. In his lecture, he focused on the control in getting things on smaller scale. Once materials are synthesized in the nanometer range, physical properties that were evidenced as confounding in the macroscopic scale diminish, and due to smaller size and shape quantum properties of these materials are influenced (Feynman 1960). Currently the field of nanotechnology is undergoing an extraordinary period of scientific and technological growth. Hence, extraordinary collaboration of a wide range of physical, biological and chemical basic science research is required to get better results at nano-level (Murty et al. 2013; Willard et al. 2004).

When size of the bulk material reduces below a certain value there is great change in material properties. Quantum effects which start to appear at this level make the properties of the material very different from its bulk properties (Murty et al. 2013). This change in properties such as electronic structure, band gap, resistance, conductivity, boiling and melting point and mechanical hardness can be utilized to make new devices and can bring a revolutionary change in the field of electronics industry, medicine, space science, environmental, and many other fields of science and technology (Willard et al. 2004). Therefore it can be defined as “the manipulation of materials measuring 100 nm or less in at least one dimension” (Kamel 2007).

1.2 Goals and Applications of Nanotechnology

Main goal of nanotechnology is the successes in the development of light weighted, small and low cost devices that use little energy and can replace huge and massive microelectronic equipment. Chemical, physical and mechanical properties of the materials at nano-level are
uniquely different as compared to that of bulk material (Murty et al. 2013). The significant use of nanotechnology is in the field of biotechnology. Nanotechnology based biosensors are one of the important devices used for site specific delivery of medicine (Vashist et al. 2012). Flexible electronic devices are the result of tremendous research in electronics at nano-level (Subramanian and Lee 2012).

Nanotechnology provides new tools for cellular and molecular biology, veterinary physiology, biotechnology and many more. Hence, engineering of food, agriculture and animal systems are the important areas in which nanotechnology can also be used (Patil et al. 2009). One of the basic humanitarian goals is the reliable access to affordable clean water and nanotechnology continuously makes available robust solution to the challenges faced during wastewater treatment (Qu et al. 2013).

Nanotechnology has applications in the field of medicine and dentistry by providing smart drugs. These help in giving faster treatment without side effects (Singh and Tawaniya 2013). Next generation is going to be exposed, directly or indirectly, to diversity of nano-products used in cosmetics, medical, sports and space science along with other various industrial applications (Murty et al. 2013).

### 1.3 Nanostructures

A nanostructure is defined as “an object of intermediate size between molecular and micrometer sized structures”. Nanostructures may occur in various different configurations on the basis of their geometry including shells, tubes, wires, rods, horns, pores, rings and belts (Murty et al. 2013; Willard et al. 2004). These nanostructures with unique geometries have novel properties and are being fabricated and synthesized for specific applications (Murty et al. 2013).

#### 1.3.1 Classification of Nanostructures

Nanostructures can be classified on various bases such as on the basis of dimensions and shapes. Three categories of nanostructures are distinguished on the bases of their shape. First one is rod shaped nanostructures, which has rod diameter in the range of few nanometers (Riaz and Naseem 2012). Second one layer shaped nanostructures and third category is formed of spherical nanometer sized nanostructures (Murty et al. 2013).
Nanostructures can be categorized into three groups on the basis of their dimensions: (1) one dimension nanostructures like thin films. These thin films have one dimension in nanometer scale. Coatings of therapeutic agents such as pills are an example of these one dimensional nanostructures. (2) Two dimensional nanostructures like nanotubes, nanorods, nanowires and fibers. The diameter of these nanostructures is in the range of 0.1 to 100nm whereas the length can be much larger. (3) Three dimensional nanostructures such as nanoparticles and quantum dots. These nanostructures have 0.1 to 100 nm size of all the three dimensions (Vashist et al. 2012).

1.4 Nanoparticles

While dealing with nanostructures, if the particle size is in the range of 1 to 100 nm and that particle acts as a complete unit in terms of its transport and properties, then these particles are called as nanoparticles (Bandyopadhyay 2008).

Properties of the nanoparticles are widely different than the properties of the same material in bulk form (Pascu et al. 2012). These nanoparticles are the nanostructures, which can fill the gap between molecular or atomic structures and bulk materials and hence are getting attention of researchers in scientific society (Santoyo Salazar et al. 2011; Šubrt et al. 2000). At nano-level size dependent properties have gained much interest as compared to the properties of the bulk material which is due to the constant physical properties of the materials in bulk form (Kreyling et al. 2006). With reduction in the dimensions of the material surface to volume ratio increased and this results in the increased reactivity of the material (Bandyopadhyay 2008). On the basis of these drastic changes in properties of nanoparticles, they are widely used in technology, science, and medical applications (Kreyling et al. 2006).

1.4.1 Potential Applications of Nanoparticles

On the basis of improved properties at nano-level, nanoparticles have potential applications in various fields. Such as, due to the larger surface area of nanoparticles, they are likely to be more biologically active as compared to the bigger sized particles with same chemical composition (Sozer and Kokini 2009). Also have been widely used in chemical sensor applications on the basis of their large surface to volume ratio and physical properties (Murty et al. 2013). On the basis of these size based properties, nanoparticles are widely used in anti-reflecting coatings, in polymer solar cells and for modification of refractive index of surfaces (You et al. 2012).
Magnetic properties of nanoparticles make them very important in high density recording media (Bomati-Miguel et al. 2014).

1.5 Iron Oxide

Iron oxides are one of the significant transition metal oxides which gained technological importance due to their application oriented properties (Cornell and Schwertmann 2003). Iron oxide holds an important place in numerous fields such as industrial and environmental chemistry, geology, physics and medicine, biology, corrosion science and in mineralogy. Hence the researchers mainly focus on the synthesis of pure iron oxide by using reliable synthesis techniques (Cornell and Schwertmann 2003). Iron oxides exist naturally in the environment and are present in organisms, in rocks and in soils, in rivers and lakes and on the seafloor (Dzade et al. 2014).

Iron oxide nanostructures are of significant interest for various applications in the field of nanotechnology such as in medicine (Lin et al. 2005), magnetic storage (Bomati-Miguel et al. 2014) and as catalyst (Kohler et al. 2005). Nanorods, hollow fibers, nanoparticles, nanowires, nanotubes and ring and snowflake like nanostructures are some of the extremely modern structures of iron oxide nanomaterials (Chirita et al. 2009).

Among these nanostructures, iron oxide nanoparticles have fascinated abundant attention during recent years, due to their technological applications like gas sensors, high density magnetic recording media, catalysts, non-linear optics, pigments, inorganic dyes, anticorrosive agents, adsorbents and in clinical uses (El Ghandoor et al. 2012; Santoyo Salazar et al. 2011; Woo et al. 2004).

1.5.1 Iron Oxide Phases

Naturally, iron oxides exist in many diverse forms and sixteen pure phases with different oxidation states of iron, composition and crystal structure (Dzade et al. 2014; Islam et al. 2011). Among these pure phases oxides like Hematite, Magnetite, Maghemite and iron oxide beta phase are of much interest (Lemine et al. 2014; Leonardi et al. 2016). Other phases particularly, hydroxides like Bernalite or Iron(III)hydroxide and Iron(II)hydroxide; oxy-hydroxides such as Akaganetite, Geothite, Feroxy-Hyte and Lepidocrocite are known to date (Ramimoghadam et al. 2014). Fe₂O₃ has four allotropic forms known as alpha (α), beta (β), gamma (γ) and epsilon (ε) with unusual relation with each other. Transition points from one to another form of these ferrites
occur at 700°C, 928°C and 1530°C, respectively. Beta form (non-magnetic) is transformed from alpha form (magnetic) without changing the lattice (Lide 1947). These compounds have distinct characteristics such as discrete colors, trivalent state and low solubility (Ramimoghadam et al. 2014). All these phases of iron oxide are crystalline except hydrous ferric oxyhydroxide (ferrihydrite) and iron oxy-hydroxy sulfate (Schwertmannite), which are poorly crystalline by nature (Cornell and Schwertmann 2003).

**TABLE 1.1: Detail of different phases of iron oxide with their properties**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Phases with formulas</th>
<th>Crystal Structure</th>
<th>Color</th>
<th>Lattice parameters (nm)</th>
<th>Formula unit/unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Wüstite (FeO)</td>
<td>Cubic</td>
<td>Black</td>
<td>a=0.4302</td>
<td>4</td>
</tr>
<tr>
<td>2.</td>
<td>Hematite (α-Fe₂O₃)</td>
<td>Hexagonal</td>
<td>Red</td>
<td>a=0.5034, c=1.3752</td>
<td>6</td>
</tr>
<tr>
<td>3.</td>
<td>Maghemite(γ-Fe₂O₃)</td>
<td>Cubic</td>
<td>Brown</td>
<td>a=0.8347</td>
<td>8</td>
</tr>
<tr>
<td>4.</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Cubic</td>
<td>Black</td>
<td>a=0.8396</td>
<td>8</td>
</tr>
<tr>
<td>5.</td>
<td>β-Fe₂O₃</td>
<td>Monoclinic</td>
<td>Yellow-brown</td>
<td>a=1.0546, c=1.0483</td>
<td>8</td>
</tr>
<tr>
<td>6.</td>
<td>ε-Fe₂O₃ (synthetic)</td>
<td>Orthorhombic</td>
<td>Red-brown</td>
<td>a=0.5095, c=0.9437</td>
<td>8</td>
</tr>
<tr>
<td>7.</td>
<td>Goethite (α-FeOOH)</td>
<td>Orthorhombic</td>
<td>Yellow-brown</td>
<td>a=0.9956, c=0.4608, b=0.879</td>
<td>8</td>
</tr>
<tr>
<td>8.</td>
<td>Akaganeite (β-FeOOH)</td>
<td>Tetragonal</td>
<td>Yellow-brown</td>
<td>a=1.0560, c=1.0483</td>
<td>8</td>
</tr>
<tr>
<td>9.</td>
<td>Lepidocrocite (γ-FeOOH)</td>
<td>Orthorhombic</td>
<td>Orange</td>
<td>a=0.3071, c=0.3873, b=1.2520</td>
<td>4</td>
</tr>
<tr>
<td>10.</td>
<td>Feroxyhyte (δ'-FeOOH)</td>
<td>Hexagonal</td>
<td>Reddish brown</td>
<td>a=0.2930, c=0.456, b=0.449</td>
<td>2</td>
</tr>
<tr>
<td>11.</td>
<td>δ-FeOOH (synthetic)</td>
<td>Hexagonal</td>
<td>Reddish brown</td>
<td>a=0.2930, c=0.449</td>
<td>1</td>
</tr>
<tr>
<td>12.</td>
<td>High pressure FeOOH</td>
<td>Orthorhombic</td>
<td>Reddish brown</td>
<td>a=0.4932, c=0.2994, b=0.4432</td>
<td>2</td>
</tr>
<tr>
<td>13.</td>
<td>Schwertmannite Fe₁₀O₁₆(CH)₉ (SO₄)₇.nH₂O</td>
<td>Tetragonal</td>
<td>Yellow-brown</td>
<td>a=1.066, c=0.604</td>
<td>2</td>
</tr>
<tr>
<td>14.</td>
<td>Ferrihydrite Fe₄HO₆.4H₂O</td>
<td>Hexagonal</td>
<td>Red brown</td>
<td>a=0.2955, c=0.937</td>
<td>4</td>
</tr>
<tr>
<td>15.</td>
<td>Fe(OH)₂</td>
<td>Hexagonal</td>
<td>White</td>
<td>a=0.3262, b=0.4596</td>
<td>1</td>
</tr>
<tr>
<td>16.</td>
<td>Bermalite Fe(OH)₃</td>
<td>Orthorhombic</td>
<td>Greenish</td>
<td>a=0.7544, b=0.7560, c=0.7558</td>
<td>8</td>
</tr>
</tbody>
</table>
These sixteen types of iron oxide and their different properties such as color, crystal structure, lattice parameters and formula units in a unit cell are given in Table 1.1 (Cornell and Schwertmann 2003).

Diversity in physical properties on the basis of chemical structure of different phases of iron oxide make them favorable in countless different applications at industrial and research level such as catalysts, magnetic recording, pigments, lubrication, coatings, ion exchangers, magnetic data storage devices, gas sensors, sorbents and in xerography (Ramimoghadam et al. 2014). Four most important phases of iron oxide are given in detail below:

1.5.1.1 Wüstite (FeO)

One of the important phases of iron oxide is Wüstite (FeO), with cubic crystal structure as shown in Figure 1.1. Wüstite is stable phase at lower pressure and high temperature of above 843K (Ramimoghadam et al. 2014).

![Figure 1.1: Crystal structure of wüstite (Yu and Zhou 2017).](image)

Closed packed fcc sub-lattice is formed by large O\(^{2-}\) anions with the small Fe\(^{2+}\) cations. All iron ions are coordinated octahedral to oxygen. Iron–oxygen bond length is 2.16 Å (Ramimoghadam et al. 2014).

1.5.1.2 Hematite (α-Fe\(_2\)O\(_3\))

Hematite is the second important and most common phase of iron oxide (Lide 1947). It has corundum (α-Al\(_2\)O\(_3\)) like structure which consists of dense arrangement of trivalent iron ions in octahedral coordination with closed hexagonal packing of oxygen atoms (Chirita et al. 2009). Hematite has hexagonal crystal system as shown in Figure 1.2 with lattice parameters a and c as
5.035 Å and 13.75 Å, respectively. The crystal structure of hematite can also be described by stacking of sheets of trivalent iron ions between two closed-packed layers of oxygen atoms, bonded together by covalent bond. In this structure only two oxygen atoms are occupied instead of available three oxygen octahedrons, which is due to the presence of trivalent state of iron (Bagheri et al. 2013). This precise arrangement results a neutral structure with no excess or deficit charge (Ramimoghadam et al. 2014). The band gap of α-Fe₂O₃ is ~2.2 eV that lies in the visible range. It possesses high refractive index. Hence, it has been studied for many optical applications, as a potential candidate, such as in photo-catalysis, solar energy conversion (Shinde et al. 2011), photo-oxidation of water, electro-chromism and in interference filters (Budas et al. 2015).

Figure 1.2: Crystal structure of Hematite (Yu and Zhou 2017).

1.5.1.3 Maghemite (γ-Fe₂O₃)

Maghemite, (γ-Fe₂O₃) is a significant magnetic material, red brown in color and a ferromagnetic mineral and it is also the 2nd most stable phase of iron oxide. Crystal structure of magnetite is given in Figure 1.3 with lattice constant 0.8350 nm close to that of magnetite (Abe and Watanabe 2014). Maghemite nanoparticles are extensively employed in biomedical applications, since their magnetism permits handling with external magnetic fields.
These particles are compatible and potentially non-hazardous to humans (Lévy et al. 2008; Pankhurst et al. 2003). It is iso-structural with magnetite, but with Iron(II) deficient sites. Its structure can be achieved by generating 8/3 vacancies out of the 24 iron sites in the cubic unit cell of magnetite and so its formula is \((\text{Fe}^{3+})_8[\text{Fe}^{3+}40/3\square8/3]_{16}\text{O}_{32}\) where \(\square\) represents a vacancy, parenthesis and square bracket indicate tetrahedral and octahedral positions respectively (Hu et al. 2011; Waychunas 1991).

Maghemite have the advantages of being the single iron oxide that exhibits both semiconducting and ferri-magnetic behavior. It is really difficult to synthesize maghemite by physical methods as it is thermodynamically metastable phase, and at 673K permanently transforms to hematite (Abe and Watanabe 2014).

1.5.1.4 Magnetite (Fe₃O₄)

Magnetite is the most essential phase of iron oxide. It is ferromagnetic and appears in black color and contains both Fe³⁺ and Fe²⁺ ions. It is naturally found as igneous rock (Wilhelm et al. 2003) and as black sand near banks of streams and along beaches (Lide 1947). Magnetite nanoparticles of approximately 20nm have high surface to volume ratio as compared to that of bulk and shows superparamagnetic behavior below its Curie temperature (850K). The Neel temperature for magnetite is 856K (Masrour et al. 2015). In this size range each particle is behaved as a single magnetic domain (Cornell and Schwertmann 2003).

Chemical formula of magnetite can be given as \(\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4\) (Cornell and Schwertmann 2003). The ratio of Fe(II) and Fe(III) in case of stoichiometric magnetite is equals to 0.5, while in case of non-stoichiometric magnetite, a Fe³⁺ deficient layer is resulted (Ramimoghadam et al. 2014).
Crystal structure of magnetite is an inverse spinel structure as shown in Figure 1.4, which contains 32 oxygen atoms with face-centered cubic unit cell. Edge length of unit cell is 0.839nm. In this specific crystal structure, octahedral sites are occupied by half of the Fe$^{3+}$ and Fe$^{2+}$, while tetrahedral sites are occupied by other half of the Fe$^{3+}$. In order to get higher energy for crystal field stabilization, Fe(II) atoms prefer to take octahedral sites. However, in case of Fe(III) atoms, crystal filed stabilization energy is zero due to which they occupy the tetrahedral and octahedral sites (Ramimoghadam et al. 2014). It has high conductivity of approximately 250 Ω$^{-1}$ cm$^{-1}$ which is due to the partially filled 3d band of the iron atoms at B site. Verwey transition is one of the important transitions of the magnetite which is a metal to insulator transition at 120K.

![Figure 1.4: Crystal structure of magnetite (Yu and Zhou 2017).](image)

Band splitting, due to electron phonon interaction and/or electron correlation, is the main reason for this structural change to monoclinic from cubic (Jeng and Guo 2002).

### 1.5.2 Iron Oxide Nanostructures

On the basis of magnetic properties, iron oxide nanostructures are widely used in numerous biochemical and biomedical applications such as protein purification, cell separation, bacterial detection, enzyme immobilization, drug delivery, MRI imaging and hyperthermia (Huang and Juang 2011).

Iron oxide nanoparticles have gained particular interest in recent years due to their enormous wide range of applications such as in magnetic hyperthermia. This, magnetic hyperthermia, is a method used for cancer treatment. The heat generated by magnetic nanoparticles when they are exposed to alternative magnetic field is the basic mechanism in this hyperthermia treatment (Lemine et al. 2014; Macher et al. 2015).
Super paramagnetic iron oxide nanoparticles are used as nano-theranostics due to their biocompatibility and magnetic features. In general, theranostics syndicates the imaging of disease and its treatment into a single formulation. These features make them perfect applicants to overcome many biological obstacles such as ineffective treatment management and poor biodistribution of drugs (Fernandez-Fernandez et al. 2011). The latest frontier in nanomedicine has been invented ‘nanotheranostics’ by which the diagnostic imaging and therapeutic capabilities of iron oxide nanoparticles are used in combination with their abilities to act as drug-carriers or as chemotherapeutic agent; take advantage of their intrinsic superparamagnetic properties (Kievit and Zhang 2011).

Iron oxide nanoparticles are extensively used as extremely active catalysts, applied in numerous acid/base and oxidation/reduction reactions, also utilized to remove toxic waste due to large surface area. These iron oxide nanoparticle catalysts can be eliminated with the help of an external magnetic field (Murty et al. 2013). Due to UV absorbing properties and durability of iron oxide nanoparticles, these are used as transparent pigments (Wang et al. 2014).

1.6 Iron Oxide based Zinc Oxide

Zinc oxide is widely used semiconductor having direct band gap with value of 3.37eV. This semiconductor has attained significant importance in research community due to its application oriented properties (Shahzad et al. 2013). Its large exciton binding energy (60 meV) is one of these important properties which results to lasing action due to exciton recombination (Anghel et al. 2010). This can take place above the room temperature. It also has higher values of breakdown voltages as well as has ability to tolerate large electric fields. The value of its electronic noise is lower with ability to work in high temperature. Low cost devices based on ZnO nanostructures can be obtained due to its modest crystal growth technology (Kang et al. 2013).

Properties (physical and chemical) of materials at nano-level are much different from those of at bulk-level. Shape and size of nanostructures with surface morphology are some factors responsible for the variation in properties of nanostructures of zinc oxide (Anghel et al. 2010). Detailed description of various properties of zinc oxide is given below.

1.6.1 Physical Properties
Due to reduction in size of bulk material below a certain value, some of the physical properties experience changes and this effect is known as quantum size effect. Table 1.2 includes some bulk properties of zinc oxide (Hong et al. 2005).

TABLE 1.2: Physical properties of bulk ZnO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant a (T=300K)</td>
<td>3.246 Å</td>
</tr>
<tr>
<td>Lattice constant c (T=300K)</td>
<td>5.206 Å</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1974.85 °C</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>8.66</td>
</tr>
<tr>
<td>Band gap Energy</td>
<td>3.4 eV (direct)</td>
</tr>
<tr>
<td>Exciton binding Energy</td>
<td>60 meV</td>
</tr>
</tbody>
</table>

As the quantum effects lead there is observable change in physical properties of nano-sized zinc oxide like increase in band gap energy is observed in case of zinc oxide nanoparticles as well as for quasi one dimensional nanostructures of ZnO. Surface states are also increased in case of nano-rods. This increase is observed by X-ray absorption spectroscopy as well as by scanning electron microscopy. This increase in surface states effects the carrier concentration also. Understanding of physical properties is much important in order to design functional devices (Ton-That et al. 2012).

1.6.2. Chemical Properties

Zincite or white powder is also known names of zinc oxide. Its crystalline form is thermochromic. It changes its color from white to yellow and vice versa upon increasing the temperature and decreasing the temperature, respectively. This change in color is due to water removal at high temperature. It is acid soluble while insoluble in alcohols and water. It results cement like product when reacts with phosphoric acid and zinc chloride (Kang et al. 2013).

1.6.3. Mechanical Properties

Mechanically it is a soft material. Its hardness is 4.5 with units of on Mohs scale. Due to this softness it has smaller elastic constants are as compared to that of other III-V semiconductors. It
has high values of heat capacity and conductivity with high melting point and low thermal expansion value (Shahzad et al. 2013).

1.6.4. Electrical Properties

Generally n-type characteristic is observed in zinc oxide, even without intentional doping. While n-type doping in zinc oxide can be easily achieved using elements belonging to group III such as In, Al, and Ga etc. On the other hand p-type characteristic can also be observed using elements of group V such as P, N and As etc. Electron mobility at 80 K has its maximum value of 2000 cm²/Vs while 5-30 cm²/Vs is the range for values of hole mobility (Hong et al. 2005).

1.6.5 Optical Properties

Zinc oxide nanostructures are extremely studied for their fundamental properties which are very essential for photonic devices. Due to these fundamental optical properties of zinc oxide its photoluminescence spectrum is intensively described in literature. Quantum confinement effect plays an important role to increase exciton’s binding energy in zinc oxide nanostructures. Blue shift near UV emission is observed due to quantum confinement in zinc oxide nanostructures. Zinc oxide nanostructures are also significant in optical switching (Ton-That et al. 2012).

1.6.6 Magnetic Properties

Zinc oxide is very worthy host material to get diluted magnetic semiconductors in order to get ferromagnetic property in semiconductors. Diluted magnetic semiconductors have received interest in research society as these semiconductors can achieve spin injection. Due to achievement of spin injection these semiconductors can overcome the incompatibility of conductance which is mostly related with simple semiconductor devices (Shahzad et al. 2013).

1.6.7 Crystal Structure

Zinc Oxide is occurred in three crystalline forms

i. Wurtzite structure

ii. Zinc blend structure

iii. Rock salt structure
1.6.7.1 Wurtzite Structure of Zinc oxide

Wurtzite structure is known as most commonly observed crystal structure of zinc oxide. This crystal structure is also known as most stable structure of zinc oxide at ambient conditions. Figure 1.5 shows hexagonal lattice structure of wurtzite zinc oxide with green circles as Zn and blue ones are showing oxygen atoms (Anghel et al. 2010).

Figure 1.5: wurtzite structure of zinc oxide (Espitia et al. 2012).

1.6.7.2 Zinc Blende Structure of Zinc oxide

Zinc-blende crystal structure is unstable form of zinc oxide which can be stabilized when grown on substrates (Kang et al. 2013). Figure 1.6 shows cubic lattice structure for zinc-blende.

Figure 1.6: Cubic crystal structure for zinc blend (Espitia et al. 2012).
1.6.7.3 Rock Salt Structure of Zinc oxide

Rock salt structure of zinc oxide is only detected at high pressure of ~ 10 G Pa (Ton-That et al. 2012). NaCl like cubic crystal structure is shown in Figure 1.7.

![Rock salt structure of zinc oxide](image)

Figure 1.7: Rock salt structure (Espitia et al. 2012).

Different crystal structure owned different properties such as pyro-electricity and piezoelectricity, both observed in hexagonal ZnO while zinc blend crystal structure shows only piezoelectricity. Reason for this variation in behavior is absence of inversion symmetry. \( a=3.25\,\text{Å} \) and \( c=5.2\,\text{Å} \) are the lattice constants for zinc oxide while \( c/a=1.60 \) is their ratio. Ideal value for this ratio is 1.633 for hexagonal unit cell. Piezoelectricity is observed in zinc oxide due to the presence of ionic bonding in zinc oxide (Hong et al. 2005).

1.6.8 Zinc oxide Nanostructures

Zinc oxide nanostructures were synthesized by various techniques and numerous morphologies of zinc oxide were observed (Ciciliati et al. 2015; Kanchana et al. 2016). Nanowires, nano-rings, nano-flowers, nano-spheres, nano-rods, and nano-belts are some of the commonly observed nanostructures of zinc oxide (Kumar et al. 2014). This variation in morphologies can be obtained with variation in synthesis conditions (Klingshirn 2007).

1.7 Goals and Objective

This research work deals with the synthesis of iron oxide nanostructures such as nanoparticles by sol-gel method with definite morphology such as particle size and size distribution. Effect of pH of the reaction in solution and doping concentration of various transition elements was studied. The density functional theory was used to study theoretical investigation of nanostructures. Iron oxide nanostructures have been familiar for their synthesis and characterization for about two decades. The chosen method of synthesis is relatively inexpensive and easy; so, there are
also feasible capacities for large-scale production. There were three primary goals that we wanted to achieve with this study. The first was to optimize the synthesis of nanostructures. The background and procedure of the actual method will come in later chapters, but it was a challenge to find the right parameters to make the reaction go as near to completion as possible to get required size and morphology on each trial.
Clearly, a reliable and repeatable technique was a necessary component for this research because it facilitates the accurate analysis of results. Once the synthesis was optimized, the next specific aim was to characterize the synthesized nanostructures. In the next goal, it is required to investigate various properties theoretically.
The final goal of this research work is to correlate the results obtained experimentally and theoretically. This correlation is important so that these nanostructures can be utilized with more accuracy in related applications.

1.8 Layout of the Thesis

The thesis is divided into 13 chapters.

In the chapter 1, the general introduction to nanotechnology, its importance, nanostructures and nanoparticles, also the detailed description about the elements chosen for the synthesis of nanostructures is given.

In the chapter 2, we address the introduction about the Density functional theory and Amsterdam density functional software, used for the theoretical studies of different properties of iron oxide nanostructures is given.

In the chapter 3, a brief summary about previous work done by various researchers for the synthesis of iron oxide nanostructures is given in first section. Theoretical work of numerous researchers is also included in the same section while second section of this chapter contains review of literature about iron oxide based nanostructures.

Chapter 4 includes experimental details about the synthesis of iron oxide based nanostructures and techniques for the characterization are also described.

In chapter 5, effect of molarity was investigated for the synthesis of different iron oxide based nanostructures. Sol-gel method was used for the synthesis.
In **chapter 6**, after optimizing molarity, effect of pH was studied and it was synthesized by sol-gel method.

**Chapter 7** includes the detailed synthesis of magnetite nanoparticles for biomedical applications.

**Chapter 8** consists of synthesis of iron oxide based nanostructures and for these structural and magnetic properties of iron doped ZnO nanostructures were investigated.

**In Chapter 9**, Mn/Fe co-doped ZnO nanostructures were investigated by studying their structural and magnetic properties.

**Chapters 10, 11, 12, 13 and 14** include theoretical results for magnetite, maghemite, hematite and wüstite phases along with iron added ZnO calculated by DFT based ADF-BAND module.
Chapter – 2  

Theoretical Background

2.1 Introduction

In the 21st century, the development of new imaging techniques and increasingly powerful computer simulations are rapidly advancing our understanding of various properties of materials at submicron scales. During recent decades, preparation and characterization of materials at nano-levels have provided the developments in physics of novel materials with reduced dimensions. Wide theoretical investigation of these innovative materials in the last decade has extended much interest.

Theoretical approaches also motivate us to gain improved or new visions into observed experimental results or to predict new physics. With the miniaturization of devices, the requirement to understand the properties on length scales below a micron is becoming increasingly important (Glotzer et al. 2017).

Various software like Object Oriented Micromagnetic Framework (OOMMF) (Liu and Fan 2014), Landau-Lifshitz-Gilbert model (LLG) (Bastrukov et al. 2012), Nmag (Kim 2010) and ADF (Hsu et al. 2011) have gained much interest of the researchers in order to study various properties of nanostructures. Among these software, ADF (Amsterdam density functional), a density functional theory based software has gained much interest due to the wide variety of applications in calculations of structural, optical and magnetic properties (Hsu et al. 2011). Some of the dynamic properties along with other details of software are given here.

2.2 Amsterdam Density Functional (ADF)

Amsterdam Density Functional (ADF) is a “FORTRAN” program for calculations in gas or solution phase on atoms and molecules. It has potential applications in many fields such as in chemistry (organic and in-organic), molecular spectroscopy and in pharma-co-chemistry for crystallography. Besides the basic ADF program, various other programs are also available in ADF package such as BAND is used to study properties of polymers, crystals and periodic surfaces. While for the investigation of thermodynamic properties of fluids COSMO-RS program can be used.

ADF software is based on density functional theory with the modifications of Kohn-Sham approach. It results in total energy and all related properties of the many–electron system in terms of exact electron density (ADF 2013).
2.2.1 Background and History of ADF

ADF software package has been developed mainly by two groups of theoretical chemists in early 1970s. First group belongs to the Vrije Universiteit in Amsterdam while second one is from the University of Calgary, Canada (ADF 2013).

At the first time it was named as HFS, later called AMOL. Due to continuous development, it made its place in the field of research.

2.2.3 Basic Programs in ADF

There are nine (9) programs or modules in this ADF software, given as

1. ADF (Amsterdam density function)
2. BAND (Amsterdam Density Functional band-structure program)
3. DFTB (Temperature dependent Density Functional program)
4. MM (Molecular Mechanics)
5. Open Babel
6. QMMM (Quantum Mechanics / Molecular Mechanics)
7. Quil (Quantum-regions Interconnected by Local Descriptions)
8. ReaxFF (reax Force Field)
9. UFF (Universal Force Field)

2.2.4 Measuring Properties/Calculations by ADF

The following calculations can be performed by using ADF.

Single point calculations along with geometry optimization can be performed. Reaction path can be traced. Thermodynamic properties can also be studied with frequencies. Various optical and magnetic properties can be studied along with electronic configuration (ADF 2013).

2.2.5 Applicability

The main advantage of ADF is that it is applicable to all elements (Z = 1-118) of the periodic table. Software database contains specific basis sets for each element. These basis sets are in different ranges from low to high quality with different sizes according to the requirement of different elements (ADF 2013).
2.3 BAND

BAND is a program used for the calculations of electronic structures of periodic systems. This program is also based on density functional theory. “FORTRAN” is the programming language for this program. For the calculations of the band structures of nanostructures, atomic units of length and energy are taken as Bohr and Hartree, respectively (Baerends et al. 2013; Velde 1990). BAND is grounded on similar theoretical model as per the Amsterdam Density Functional program. General set up for these two is also similar (Velde 1990).

2.3.1 Functionality and Applicability

By using BAND, a periodic system of any type can be handled. As a result the system is called “n” dimensional crystal system. Polymer, slab and bulk crystals are examples of this crystal system with n equals to 1, 2 and 3 dimensional respectively.

Major advantage of using BAND is that the spin-restricted and unrestricted calculations can be performed by treating two spins independently. Different formulas like Gunnarsson-Lundqvist (GL), the classical Xa and Vosko-Wilk-Nusair (VWN) can be applied for calculations of exchange correlation potential (VXC).

The program calculates cohesive and total energies and X-ray factors. Partial and total density of states along with calculations for Mulliken population analysis is also one of the best reported results of BAND (Velde 1990). Voronoi Deformation Charges can be obtained by using Voronoi cells for charge analysis along with Hirshfeld charge analysis. Orbital and deformation density plots are also studied. To study the band gap of the crystal systems band structure plots with boundaries of the Brillouin zone can also be plotted by using BAND program (ADF 2013).

2.3.2 Formalism

Main achievement in Kohn-Sham theory for the density functional method is the replacement of two-particle coulomb interaction (1/r) between electrons by the sum of two operators. Among these two operators, Coulomb potential is the first one which is due to the average charge distribution while exchange-correlation (XC) potential is the second one (Hohenberg and Kohn 1964; Kohn and Sham 1965). Exchange-correlation (XC) potential represents the correlation and exchange effects in balanced way. It is used as a functional for charge distribution (Velde 1990). The basic Hamiltonian equation is given in Equation (2.1) with typical approximation of static point nuclei as:
\[ H\psi_n(k;\mathbf{r}) = \{ T + V_C(\mathbf{r}) + V_{XC}(\mathbf{r}) \} \psi_n(k;\mathbf{r}) = e_n(k) \psi_n(k;\mathbf{r}) \]  

(2.1)

Where, \( T \) is the operator for kinetic energy, \( V_{XC}(\mathbf{r}) \) is the xc potential and \( V \) is the total coulomb potential. This total coulomb potential is due to the electron cloud and nuclear charges. In BAND relativistic effects have not been included yet. While, \( \Psi_n(k;\mathbf{r}) \) is a one-electron state containing wave vector \( \mathbf{K} \). \( \mathbf{K} \) also serves as symmetry label. It is a variable which may assume all values in the first Brillouin Zone (Velde 1990). The solutions \( \{ e_n(k), \psi_n(k;\mathbf{r}) \} \) vary continuously with \( \mathbf{K} \) and thus form bands. The subscript \( n \) is called band index and computes the distinct solutions in \( k \). The translation properties of \( k \), as given in Equation (2.2), were stated for the first time in Bloch’s theorem in 1929 (Bloch 1929).

\[ \psi = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_n(k;\mathbf{r}) \]  

(2.2)

In Equation 2.2, \( \mathbf{R} \) indicates any point of Bravais lattice. The electronic charge density is represented by \( \rho(\mathbf{r}) \) and is obtained by a summation terminated to all occupied states. Integration in \( k \)-space is included in summation as given in Equation (2.3).

\[ \rho(\mathbf{r}) = \sum_n \int_{BZ} \mathbf{d} \mathbf{k} \left| \psi_n(k;\mathbf{r}) \right|^2 \theta(e_F - e_n(k)) \]  

(2.3)

While the fermi energy \( e_F \) is calculated by total amount of electronic charge (Q) per unit cell as shown in Equation (2.4) (Velde 1990)

\[ \rho(\mathbf{r}) \mathbf{d} \mathbf{r} = Q \]  

(2.4)

**2.3.3 Starting up with sub Program DIRAC**

BAND contains a subprogram named “DIRAC” which is completely like numerical Herman-Skillman subprogram (Herman and Skillman 1963). This subprogram DIRAC is used to solve equations of density functional for free atoms with spherical symmetry. The crystal is built up from these free atoms. Self-consistency iterations for described crystal are started up by super positioned atomic densities along with corresponding potential. Calculations of cohesive energies are performed with respect to these atoms. Different properties like orbitals, coulomb potential and atomic density are calculated by DIRAC and all the calculated data is represented in the form of tables (Velde 1990).
2.3.4 Basis and Basis Sets

BAND involves two different types of basis functions. One is the Bloch functions (Bloch 1929). These are calculated as linear permutations of localized functions and can be represented as in Equation (2.5)

$$\phi(k;r) = \sum_R e^{ik \cdot R} \chi(r-R)$$  \hspace{1cm} (2.5)

Where $e^{ik \cdot R}$ is the phase factors which assures that $\phi(k;r)$ attains correct translational symmetry as in Equation (2.2). Plane wave is the second type of integrals used in BAND. These are used solitary for 3-dimensional crystals because in systems other than 3 dimensions the asymptotic behavior is inappropriate to define bound electron states (Velde 1990). Basis functions involve Numerical Orbitals and/or Slater-Type Orbitals. On the basis of these functional, six different basis sets are used in the program for different systems (ADF 2013).

2.3.5 Frozen Core Approximations

Frozen core approximation is one important parameter and is widely used in DFT calculations because size of basis set is reduced due to its usage. This results in minimum computer time (Van Lenthe and Baerends 2003).

2.3.6 Poisson’s Equation

The coulomb potential is represented as $V_C(r)$ and is due to electronic density $\rho(r)$ and nuclear charges $Z_\alpha$. This coulomb potential is defined in program as Equation (2.6).

$$V_C(r) = \int [\rho(r) + \sum_\alpha Z_\alpha \delta(r-r_\alpha)] \frac{1}{|r-r'|} \, dr'$$  \hspace{1cm} (2.6)

The coulomb potentials $V_C(r)$ are obtained from DIRAC in the form of tables. This potential is due to atomic densities $\rho_\alpha(r)$ and nuclei $Z_\alpha$. Deformation density $\rho_{\text{def}}(r)$ is defined as “the difference between superposition of atomic densities and crystal charge distribution”. By using these two, Equation (2.6) results as:

$$V_C(r) = \sum_\alpha V_\alpha(r) + \int \rho_{\text{def}}(r') \frac{1}{|r-r'|} \, dr'$$  \hspace{1cm} (2.7)
In Equation (2.7), when $\rho_{\text{def}}(r)$ is attained, this form prevents analytical calculation of the second term. This results in unsuitability of normal numerical integration. Baerends et al. (1973) solved this problem by fitting procedure. A set of fit functions is selected such that the density in Equation (2.7) can be expanded accurately in them and corresponding coulomb potentials can also be evaluated easily (Baerends et al. 1973).

By fitting this functional coulomb potential is represented by this modified form given in Equation (2.8).

$$V_C(r) \approx \sum_{\alpha} V_\alpha + \sum_i c_i f_i^C(r)$$  \hspace{1cm} (2.8)

BAND is based on the Density functional theory (DFT) as by evaluating density of the system, energy of the system can be calculated.

### 2.4 Density Functional Theory (DFT)

Density functional theory (DFT) has gained much attention for the past 30 years and became dominant method for the theoretical investigation of periodic systems (Parr 1980). Further research in this theory makes it useful to investigate energy surfaces of various molecules (Levine 2013). Density functional theory tries to calculate ground state energy ($E_0$) along with other molecular properties at ground state from electron density at ground state ($\rho_0$) (Ermakov et al. 2013; Levine 2013).

#### 2.4.1 Motivation for DFT with Solution of Schrödinger Equation

Calculation of ground state energy of atoms in periodic arrangement is the primary concern dealing with the density functional theory. This ground state energy can be calculated by using solution to the Schrödinger equation (Saleem 2015). Schrödinger equation in nonrelativistic and time independent mode with Born-Oppenheimer approximation is given as in Equation (2.9) (Parr 1980).

$$\hat{H}\Psi (r_1, r_2, \ldots, r_N) = E\Psi (r_1, r_2, \ldots, r_N)$$  \hspace{1cm} (2.9)

Where, $\hat{H}$ is the Hamiltonian operator, $E$ is energy eigenvalue and $\Psi$ is the wave function. Hamiltonian operator in this equation is the sum of three terms given as in Equation (2.10).
\[ H = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + V_{\text{ext}} + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \]  

(2.10)

In Equation (2.10), first term represents kinetic energy, while \( V_{\text{ee}} \) is the electron-electron interaction and third term gives interaction with the external potential (\( V_{\text{ext}} \)). In simulation of materials this external potential is defined as the interaction of atomic nuclei with electrons and given as in Equation (2.11).

\[ V_{\text{ext}} = -\sum_{\alpha}^{N_{\text{at}}} \frac{Z_{\alpha}}{|\mathbf{r}_{i} - \mathbf{R}_{\alpha}|} \]  

(2.11)

Where, \( r_{i} \) is the coordination number of \( i \)th electron and \( Z_{\alpha} \) is the nucleus charge at \( \mathbf{R}_{\alpha} \). A set of wave function (\( \Psi \)) is used to solve Equation (2.9). For this it is assumed that wave function (\( \Psi \)) can change sign when coordinates of two electrons are interchanged. That means it is antisymmetric in nature (Kirkpatrick \textit{et al.} 1999). Ground state energy (\( E_{0} \)) for an electron is represented by the lowest energy eigenvalue. \(|\Psi_{0}|^2\) is the probability density used to find an electron with a set of specific coordinates \( \{r_{i}\} \). Expected value of \( \hat{H} \), calculated by using particular wave function (\( \Psi \)), gives average total energy for a state for that particular wave function and given in Equation (2.12).

\[ E[\Psi] = \int \Psi^{*} \hat{H} \Psi \, d\mathbf{r} = \langle \Psi | \hat{H} | \Psi \rangle \]  

(2.12)

The term \(|\Psi|\) represents that the calculated energy is a functional of the wave function (\( \Psi \)). The ground state energy is less than average total energy excepting the condition when \( \Psi \) corresponds to \( \Psi_{0} \), represented by variational theorem as in Equation (2.13).

\[ E[\Psi] \geq E_{0} \]  

(2.13)

Ground state energy and wave function for this energy can be found by calculating all possible wave functions. Hartree-Fock theory states that structure of wave function is antisymmetric and defines it as product of functions (\( f_{i} \)), while each of these functions (\( f_{i} \)) depends on the coordinates of single electron in periodic system.

\[ \Psi_{\text{HF}} = \frac{1}{\sqrt{N!}} \text{det}[\phi_{1} \phi_{2} \phi_{3} \ldots \phi_{N}] \]  

(2.14)
Where, in Equation (2.14) det specifies a matrix determinant (Szabo and Ostlund 2012). Expression for Hartree Fock energy can be calculated by using this assumption of Hartree Fock theory for $\Psi$ in Schrödinger equation (2.16).

$$
E_{HF} = \int \phi_i^*(r) \left( -\frac{1}{2} \sum_{l=1}^{N} \nabla_l^2 + V_{ext} \right) \phi_i(r) dr \\
+ \frac{1}{2} \sum_{l,j}^{N} \int \frac{\phi_i^*(r_1)\phi_l(r_1)\phi_j^*(r_2)\phi_j(r_2)}{|r_1 - r_2|} dr_1 dr_2 \\
- \frac{1}{2} \sum_{l,j}^{N} \int \frac{\phi_i^*(r_1)\phi_l(r_1)\phi_j(r_2)}{|r_1 - r_2|} \phi_j^*(r_2) \phi_l(r_2) dr_1 dr_2
$$

(2.14)

In Equation (2.15), second and third terms are classical Coulomb energy and exchange energy, respectively. Classical Coulomb energy is given in terms of orbitals. Variation theorem was applied to the above energy expression in order to calculate ground state orbitals. In above calculations, orbitals are assumed to be orthonormal. As a result Hartree-Fock equations is obtained as shown in Equation (2.16).

$$
\left[-\frac{1}{2} \nabla^2 + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' \right] \phi_i(r) + \int v_X(r,r')\phi_i(r') dr' = \epsilon_i \phi_i(r)
$$

(2.16)

Where $v_x$ is the non-local exchange potential, given as in Equation (2.17).

$$
\int v_X(r,r')\phi_i(r') dr' = -\sum_{l=1}^{N} \int \frac{\phi_i^*(r)\phi_l(r')}{|r-r'|} \phi_l(r') dr'
$$

(2.17)

Equation (2.16) gives details of electrons, which gives non-interacting behavior due to the effect of field potential. This potential consists of non-local exchange potential and classical Coulomb potential.

By using all these calculations and approximations for wave function ground state energy and total energy can be calculated but in all these calculations the computational cost is very high and limitation of number of electrons is also observed (Szabo and Ostlund 2012). Besides these problems addition of basis set adds more expense to give accurate results for calculations. For molecular calculations many correlated methods have been studied such as MP4, CCSD and CISD methods. The cost for these methods depends on the number of electrons on which these
calculations have done. In these methods CCSD (T) is the method, which gives accurate results for chemical properties such as reaction rate and stability etc. Due to all these expenses, all these methods lack interest of researchers (Hammond et al. 1994).

Hence, in condensed matter science, direct solution to Schrödinger Equation is not easily possible due to all the problems discussed above. This lack of solution is the undeviating motivation behind the density functional theory (Saleem 2015).

2.4.2 Neglecting the Solution of the Schrödinger Equation

In Equation (2.10) the Hamiltonian operator deals with the interaction of single electron and bi-electron which indicate the use of coordinates of one or two electrons only (Saleem 2015).

In order to calculate the total energy, it is not essential to find the 3N dimensional wave function. In this case, it is important to know the probability density of two particle systems. This probability density gives the probability of finding two electrons, one at \( r_1 \) and other at \( r_2 \), respectively. Hence in order to find the energy, second order density matrix plays an important role which is given as in Equation (2.18).

\[
P_2(r'_1, r'_2; r_1, r_2) = \frac{N(N-1)}{2} \int \Psi^*(r'_1, r'_2, \ldots, r'_N) \Psi(r_1, r_2, \ldots, r_N) dr_3 dr_4 \ldots dr_N
\]

(2.18)

Pair density or two particle density matrix, also shown as diagonal elements of \( P_2 \) in Equation (2.18) are given as:

\[
P_2(r_1, r_2) = P_2(r_1, r_2; r_2, r_1)
\]

This results in two electron probability function which helps in finding operators for two particles. In the same manner the first order density matrix can be defined and written as in Equation (2.19).

\[
P_1(r'_1; r_1) = \frac{2}{N-1} \int P_2(r_1 r_2; r_1 r_2) dr_2
\]

(2.19)

Total energy can be determined exactly by given \( P_1 \) and \( P_2 \) as in Equation (2.20).
\[ E = \text{tr}[\hat{H}\hat{P}] \int \left[ \left( -\frac{1}{2}\nabla_i^2 - \sum_{\alpha}^{\text{Nat}} \frac{Z_{\alpha}}{|r_{\alpha} - R_{\alpha}|} \right) P_1(r_{1}',r_{1}) \right] dr_1 + \int \frac{1}{|r_1 - r_2|} P_2(r_1,r_2)dr_1dr_2 \]

(2.20)

From these calculations we can conclude that the total energy can be determined ‘by diagonal elements of the first and second order density matrices’. This seems to vastly streamline the task in hand. So, it is not compulsory to find solution of the Schrödinger equation for wave function \( \Psi \). Total energy can be calculated by only finding \( P_1 \) and \( P_2 \). Hence, the problem in a space of 3N coordinates has been reduced to a problem in a 6 dimensional space.

There are certain problems in using approaches constructed on the direct minimization of \( E(P_1,P_2) \). One of them is the construction of density matrices from a wave function which is antisymmetric. This consideration is much important and hence still remains as unsolved problem (Erdahl and Smith Jr 2012). From all the above discussion, we conclude that it is difficult to find the total energy without finding many body wave functions and therefore Equation (2.20) does not indicate a reliable method for calculating the total energy. The plus point in using density functional theory is that we can even find total energy without calculating \( P_2 \). Hence, only charge density i.e. only first order density matrix can be used to calculate ground state energy in case of density functional theory.

### 2.4.3 The Hohenburg-Kohn Theorems

Pierre Hohenburg and Walter Kohn, in 1964 proved that wave function, molecular energy and many molecular electronic properties at ground state can be uniquely determined by calculating electron probability density of molecules having nondegenerate ground state (Hohenberg and Kohn 1964). The required electron probability density is at ground state and is functional of three variables only i.e. \( \rho_0(x, y, z) \), where subscript zero is specified for ground state (Levine 2013). In this regard they proved two theorems (Hohenberg and Kohn 1964). The first theorem can be defined as:

“The electron density determines the external potential (to within an additive constant).”

If this is true then it directly follows that the Hamiltonian operator, given in Equation (2.10), can be uniquely determined by electron density. This can be calculated by integration of density over all space. While, Hamiltonian is calculated by total number of electrons (N) and external potential (Saleem 2015). Hence, in principle, Hamiltonian operator can be determined from charge density. From this operator wave functions of all states can be calculated and as a result all properties of the materials can be computed (Saleem 2015). Straightforward proof of this
theorem was given by Hohenburg and Kohn but Levy gives proofs of its generalized form for systems with degenerate states in 1979 (Hohenberg and Kohn 1964; Lévy et al. 2008). Basically, introduction and proof of this theorem was also put forward by theoretical spectroscopist E. B. Wilson in 1965 during a meeting. Wilson’s observation was that the electron density inconsequentially gives Hamiltonian by uniquely determination of charges and positions of the nuclei. This proof is obvious and sophisticated that shows its dependency on the fact that the electron density has a limit at the nucleus, which is given as (Saleem 2015):

\[ Z_{\alpha} = \frac{-1}{2\bar{\rho}(0)} \left[ \frac{\delta \bar{\rho}(r_{\alpha})}{\delta r_{\alpha}} \right]_{r_{\alpha}=0} \]

Here, \( \bar{\rho}(r) \) is the spherical average of \( \rho \). Hence, careful calculations of the charge density exclusively regulate the external potential and therefore the Hamiltonian. Although it is not much general as compared to the Levy proof, but it results in the establishment of theorem dealing with electrons with nuclei. Hence the first theorem can be summarized as “energy is a functional of density i.e. \( E[\rho] \)” (Saleem 2015).

Hohenburg and Kohn’s second theorem results in a variational principle. “For any positive definite trial density, \( \rho_t \), such that \( \int \rho_t (r) \, dr = N \) then \( E[\rho_t] \geq E_0 \)” (Saleem 2015).

We know from the first theorem that trial wave function (\( \Psi_t \)) and single trial Hamiltonian (\( H_t \)) can be calculated from trial density i.e. \( E[\rho_t] = \langle \Psi_t | H | \Psi_t \rangle \geq E_0 \) follows instantly from the variational theorem based on the Schrödinger equation as given in Equation (2.13). This theorem limits DFT to studies of the ground state. From these two theorems, the fundamental statement of density functional theory can be given as in Equation (2.21).

\[ 7m[E[\rho]] - \mu(\int \chi(r) dr - N) = 0 \quad (2.21) \]

Density and ground state energy resembles to minimum of some functional \( E[\rho] \) subject to the limitation that the density contains the correct number of electrons. Electronic chemical potential is represented as \( \mu \) and is constraint of Lagrange multiplier. A remarkable fact can be established from the above discussion that there exists a universal functional \( E[\rho] \). This functional is independent of the external potential. Which means total energy and precise ground state energy can be calculated by calculating the value of this functional (Catlow 2003).
2.5 The Energy Functional

It was observed from Equation (2.9) (Schrodinger equation) that three terms combine to give energy functional. Kinetic energy, electron-electron interaction and interaction with the external potential are these three terms making the final form of energy potential as given in Equation (2.22).

\[ E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_{\text{ee}}[\rho] \]  

(2.22)

In Equation (2.22), second term, interaction with the external potential, is insignificant. Electron-electron and kinetic energy functional are unknown. Minimized energy can be obtained by finding good approximations to these two functional (Foley and Madden 1996).

Kohn and Sham in 1956 proposed an approach for the approximation of electron-electron and kinetic functional (Kohn and Sham 1965). They introduced an imaginary system of N electrons which are non-interacting and this system can be described by wave function with single determinant in N orbitals. From these orbitals of the system electron density and kinetic energy can be calculated exactly as given in Equation (2.23).

\[ T_s[\rho] = -\frac{1}{2} \sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle \]  

(2.23)

While, accurate ground state density can be calculated by Equation (2.24).

\[ \rho(r) = \sum_i |\phi_i|^2 \]  

(2.24)

The calculation of the exact density unambiguously from a set of orbitals confirms that it is authorized which indicates it’s calculations from a wave function that is asymmetric. Hartree energy or classical Coulomb interaction is the major module of electron-electron interaction. This is simply represented in terms of density in the second term of Equation (2.15).

\[ V_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \]  

(2.25)

By using Equation (2.25), the rearranged form of energy functional is given in Equation (2.26).

\[ E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + V_H[\rho] + E_{\text{xc}}[\rho] \]  

(2.26)
Exchange-correlation functional is also introduced as given in Equation (2.27).

\[ E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho]) \quad (2.27) \]

Where, \( E_{xc} \) is basically the sum of two errors. First one made while using kinetic energy which is non-interacting and second is while treating classical electron-electron interaction. We can write Equation (2.28), which gives the final equation for orbitals giving the minimized energy, by combining Equations (2.26), (2.24) and (2.21).

\[
\left[ -\frac{1}{2} \nabla^2 + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r) \quad (2.28)
\]

Where \( V_{xc} \) in Equation (2.28) is local multiplicative potential and is defined as “the functional derivative of the exchange correlation energy with respect to the density” given in Equation (2.29) (Levine 2013).

\[ V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (2.29) \]

These Kohn-Sham equations explain the performance of electrons (non-interacting) in an operative local potential. These equations have the similar structure as of Hartree-Fock equations (Equation 2.16). The Kohn-Sham method attains a precise calculation for the ground state density and density of a system containing non-interacting Fermions also for actual many body system defined by Schrödinger equation. The calculation of exact value of energy and charge density of the non-interacting and many-body system is only possible by knowing the exact functional. In this regard Kohn-Sham DFT is a realistic methodology. For any specific system we can solve the Schrödinger equation accurately and calculate the energy functional along with potential associated with it. This contains a larger effort as compared to in getting energy by direct solution. This property of finding exact solution for such systems is usually related with an ab initio theory. Due to this the approximations to density functional theory debated here are frequently referred to as first principles or ab initio methods. In practice, the usefulness of the theory depends on the approximation used for \( \text{Exc}[\rho] \) (Catlow 2003).
Construction of approximations for $E_{xc}$ is still promptly expanding research field. Different types of many functionals are available now with more or less accuracy for any specific system. Final judgments can be made on the basis of results but awareness of the structure and derivation of functionals is very important while selecting the approximations for particular study. Two different approximations named Local density approximation (LDA) and Generalized gradient approximation (GGA) are mostly used for exchange potential. Detail of these approximations is given below (Catlow 2003).

### 2.5.1 Local Density Approximation (LDA)

The easiest and simplest to use approximation in density functional approximations is local density approximation (LDA) in which “the functional is a simple integral over a function of the density at each point in space”. Mathematically it can be expressed as in Equation (2.29). As, this functional only involves the value of density at $r$, therefore it is called as local functional (Levine 2013).

$$E_{xc}^{loc}[n] = \int d^3 r f(n(r))$$  \hspace{1cm} (2.29)

Where, $f(n(r))$ is any function of $n(r)$.

In 1965, Kohn and Sham introduced most successful approximation to exchange correlation, named as local density approximation. Till the early 90s, it was used as a standard and reliable approximation for all density functional calculations (Burke 2007).

Initially practical applications of density functional theory were mainly for one specific system for which nearly precise results were obtained. The electrons in that system were subjected to external potential, which is constant and results in constant charge density. Hence, this system is consequently identified by constant electron density given by $\rho=N/V$ (Catlow 2003). In early 1920’s, Thomas and Fermi studied the homogeneous electron gas (Fermi 1927; Thomas 1927). The system’s orbitals are plane waves by symmetry. They considered that total energy functional could be computed when electron-electron interaction was estimated by the Hartree potential. Classically, it simply means neglecting correlation and exchange effects (Fermi 1927; Thomas 1927). On the basis of these conditions, exchange and kinetic energy (Equation 2.15) became independent of density of the electron gas (Dirac 1930; Lieb 1981) and can be represented in expressions of local functions of density. This recommends that approximate functional, in case of inhomogeneous system, can be an integral above a local function. Equation (2.30) indicates
the usage of exchange and kinetic energy densities of homogeneous electron gas (non-interacting);

\[ T[\rho] = 2.87 \int \rho^{5/3}(r) dr \]

And,

\[ E_x[\rho] = 0.74 \int \rho^{4/3}(r) dr \quad (2.30) \]

These results are extremely suggestive of a demonstration for \( E_{xc} \) in non-interacting inhomogeneous system. Hence, approximation for local exchange correlation energy can be expressed as Equation (2.31).

\[ E_{xc}[\rho] \approx \int \rho(r) \epsilon_{xc}(\rho(r)) dr \quad (2.31) \]

This shows that the local density approximation is the obvious choice. The value of \( \epsilon_{xc}(\rho) \) in LDA is a function of simply the density with its local value. It can be represented into correlation and exchange contributions as shown in Equation (2.32).

\[ \epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho) \quad (2.32) \]

Equation (2.33) gives the Dirac form for \( \epsilon_x \) (Equation 2.30).

\[ \epsilon_x(\rho) = -C \rho^{1/3} \quad (2.33) \]

Where, \( C \) is a free constant. This is the widely applicable form of functional as compared to that obscure by its derivation (Parr 1980).

### 2.5.1.1 Disadvantages of Local Density Approximation

In general LDA works on the rule of quite gentle cancellations between correlation and exchange interactions (Catlow 2003). By using LDA for molecules and even for atoms, total exchange energy of 10% is typically underestimated, while the correlation energy by a factor of 2 or 3 are overestimated by using LDA. Hence, typical underestimation of about 7% is observed in final
exchange correlation energy. In case of solids band gap structures are obtained by plotting these eigenvalues. For these calculations the overall position and shape is good but the band gap between lowest unoccupied molecular orbital (LOMU) and Highest unoccupied molecular orbitals (LUMO) is steadily underestimated by a minimum factor of 2. Hence in case of some semiconductors, when we use LDA, they do not show any band gap. This results in wrong prediction of their metal nature on the basis of their band structure. Specifically in case of solid state physics, while dealing iron an infamous failure is observed which states that magnetic structure of iron have higher energy as compared to those of non-magnetic one (Burke 2007).

2.5.2 Generalized Gradient Approximation (GGA)

LDA is established for the systems where density (ρ) fluctuates gradually with position, following the basic model for uniform electron gas (Levine 2013). In this case $E_{xc}$ is only functional of $\rho$. In order to get improved functional i.e. which can work for variation of density with position. These improved functional can be obtained in a simple way by adding gradients of densities of spin $\alpha$-electrons ($\rho^\alpha$) and spin $\beta$ electrons ($\rho^\beta$) in the integrand (Levine 2013).

A functional form is implemented in generalized gradient approximation (GGA). This form confirms the condition of normalization (Perdew and Yue 1986; Perdew et al. 1991). This results to an energy functional which depends on two terms a) the density and b) its gradient. The representative form for a GGA functional is given in Equation (2.34).

$$E_{xc} \approx \int \rho(r)\epsilon_{xc}(\rho, \nabla \rho)dr \quad (2.34)$$

Binding energy of the molecules can be accurately calculated by using GGA as compared to LDA and this makes it widely used approximation in various fields such as in chemistry community. As a result within the GGA a number of functionals have been developed (Becke 1988b; Langreth and Mehl 1983; Lee et al. 1988; Perdew et al. 1996). Some commonly used exchange functionals in GGA are PWx 86 or PW 86 Perdew and Wang’s 1986 and 1991, Becke’s 1988, B88 or B and PWx91. While some correlation functionals are Perdew (PWc 91) and Lee Yang Parr (LYP). PBE which is Perdew Burke Ernzerhof is the exchange as well as correlational functional which does not have empirical parameters. This functional is widely used in the calculations of solids on the basis of density functional theory. These functional used in GGA are called semi-local functional as they contain the values of $\rho$ in a minute neighborhood of $r$ along with at $r$ (Levine 2013).
2.5.3 Meta-GGA Functional

GGA functionals depend on ground state density $\rho$ and its first derivative. Improved or advanced GGA functional can be obtained by getting functional which can also depend on kinetic energy density or second derivative of probability density $\rho$. These improved functionals are named as meta-GGA functionals (Levine 2013). These functionals depend overtly on the semi-local statistics in the spin Laplacian (Neumann and Handy 1997; Perdew et al. 1999; Tschinke and Ziegler 1989). The form of the meta-GGA functional is typically represented as given in Equation (2.35).

$$E_{xc} \approx \int \rho(r)\varepsilon_{xc}(\rho, |\nabla \rho|, \nabla^2 \rho, \tau) \, dr$$  \hspace{1cm} (2.35)

While “$\tau$” represents the kinetic energy density and given as in Equation (2.36);

$$\tau = \frac{1}{2} \sum_i |\nabla \Phi_i|^2$$  \hspace{1cm} (2.36)

Where, $\Phi_i$ is Kohn-Sham orbitals used for the electrons with $\alpha$-spin while the sum drives over all the occupied orbitals. DFT calculations using meta-GGA require much more time as compared to that done by using GGA (Levine 2013).

2.5.4 Hybrid Exchange Functional

A hybrid functional first proposed by Becke in 1993 was used to define new functional (Becke 1988a). This functional is with coefficients which are determined by a fit to the detected ionization potential, atomization energies and proton affinities with total atomic energies for small molecules (Becke 1993). The subsequent energy functional is given in Equation (2.37).

$$E_{xc} = E_{xc}^{LDA} + 0.2(E_{X}^{\text{Fock}} - E_{X}^{\text{LDA}}) + 0.72\Delta E_{X}^{B88} + 0.81\Delta E_{c}^{PW91}$$  \hspace{1cm} (2.37)

Where $\Delta E_{c}^{PW91}$ and $\Delta E_{X}^{B88}$ gives widely used GGA corrections to the LDA correlation and exchange energies, respectively (Becke 1998; Perdew and Wang 1992). Hybrid functionals are now very extensively used in various applications (Lee, 1988). Density fitting method is used for large molecules in order to get fast density functional calculations. When we use these hybrid functionals with density fitting, it will take more time to calculate the properties (Levine 2013).
2.6 Summary

Density functional theory gives us a relatively competent and balanced tool with which one can calculate the ground state energy in accurate models of different surfaces and bulk materials. The consistency of such calculations is governed by the improvement of approximations for the functional of exchange-correlation energy. In recent years, major advances have been made in features of the functional. Local density approximation is remarkably reliable and very simple approximation for the structure and relative phase stability of different materials. Besides these advantages it is less precise for binding energies and for transition states. On the other hand GGA functional results in accurate binding energies with typical errors of 20 kcal/mol. The relative error is of 3-7%. While this error reduces to 3-5 kcal/mol and 2-3% for meta-GGA and hybrid-exchange functional.
CHAPTER-3
Chapter – 3

3.1 Introduction

Iron oxide nanostructures have received much attention in various fields such as in biomedical applications and in spintronic devices (Gupta et al. 2010; Tewes et al. 2014). These potential applications of iron oxide nanostructures depend on the size and shape of these synthesized nanostructures as size and shape are the important parameters for their applicability (Guo et al. 2015; Kayani et al. 2014).

The significant properties of different iron oxide nanostructures are mainly dependent on the synthesis method and its various parameters such as temperature, dopant concentration and pH etc. (Lemine et al. 2012). There are various methods for the synthesis of these iron oxide nanostructures like sol-gel (Kayani et al. 2014), physical vapor deposition (Riaz and Naseem 2009) and co-precipitation (Riaz et al. 2014e). These methods along with other parameters are responsible for the diversity in shape and size of the nanostructures. Various researchers report their work about the synthesis and characterization of iron oxide nanostructures. They used various methods for the synthesis of iron oxide nanostructures along with different characterization techniques to investigate their properties.

Besides experimental techniques, theoretical investigations of these nanostructures have also gained much interest. A lot of work, focusing different properties investigating theoretically, was done by using different theories. DFT is one of these important theories which was used for the theoretical investigations of different nanostructures since last five decades (Saleem 2015). Different softwares based on this theory were used with main focus to get required properties without wastage of excess materials and time. Once we get calculations and theoretical estimates, we can achieve excellent required results experimentally, which will results in efficient devices at low cost. Hence we can use these nanostructures in various applications for the benefit of humanity.

In section I of this chapter various methods and characterization techniques used by researchers for the synthesis of different iron oxide nanostructures is discussed. Theoretical investigation of different phases of iron oxide by various softwares is given in section II of this chapter. On the basis of this review of literature, we were able to choose the method for synthesis and characterization of the synthesized nanostructures. As well as choice of accurate software was done to theoretically investigate their properties.
3.2 Experimental Investigations of Iron Oxide Nanostructures

Cannas et al. (2011) reported about the synthesis of pure maghemite nano-powders. They used sol-gel self-combustion method. They used iron nitrate as a precursor and pH was adjusted by liquor ammonia. They used citric acid and iron metal in ratio of 1:1 and synthesized nanoparticles with average size of 19 nm. pH of the gel for pure maghemite was of 7 and primer temperature was in the range of 290-325°C. They concluded that pure tetragonal maghemite phase was observed by XRD. High degree of crystallinity of nano-powder was observed by HRTEM. Presence of maghemite phase was also confirmed by Mossbauer measurements with Fe(octa):Fe(tetra) ratio of 1.62. Magnetic field dependent spin canting appeared which disappeared at 6T.

Hu et al. (2011) reported the synthesis of different phases of iron oxide such as magnetite, maghemite and hematite. They used one step microwave assisted autoclave method to synthesize iron oxide nanoparticles. FeCl₂ and FeCl₃ were used as precursors and a solution of ethanol and water was used as solvent. NaOH was used as a base. Synthesized nanoparticles were characterized by using X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). They concluded that maghemite or magnetite nanoparticles were synthesized by using FeCl₂ as single precursor. Maghemite and magnetite phases depend on drying conditions. Pure hematite phase was obtained with FeCl₃, while by using both salts of iron chloride they synthesized pure maghemite. The particle size in each case depends on the synthesis conditions.

Salazar et al. (2011) reported about the synthesis of magnetite iron oxide nanoparticles by using hydrothermal method in the presence of argon. They investigated the effect of pH and ratio of iron to length of alkyl chain on the size of the synthesized nanoparticles. They used iron chloride hexahydrate and iron chloride tetrahydrate as precursors and ammonium bases to synthesize nanoparticles in the range of 10-40 nm. Magnetite nanoparticles of 12nm were observed with swift increase of pH from acidic to basic level. Homogenous growth was observed at 250 °C during hydrothermal treatment in case of greater than 3.5 ratios of iron and base. They concluded that smaller particle size was observed when longer alkyl chains were used with more basic pH. Zero field and field cooling curves showed that nanoparticles with size greater than 20nm revealed Verwey transition at 120 K, which is the characteristic of magnetite. They used core-shell model in order to describe nanoparticles in which close to maghemite an oxidized layer
surrounded the magnetite core. Below 20nm they observed that the decreased particle size resulted in increased fractional volume of maghemite.

Ghandoor *et al.* (2012) reported about the synthesis of Fe$_3$O$_4$ nanoparticles by using co-precipitation method. They used ferric and ferrous solutions for the synthesis. They also synthesized non-aqueous magnetic fluid which was stable and contained Fe$_3$O$_4$ nanoparticles. These nanoparticles were of superparamagnetic nature with diameter of 10nm. X-ray diffraction (XRD), vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM) were used to study the structural and magnetic properties of the nanoparticles and magnetic fluid. They concluded from the calculated band gap parameters like direct and indirect-band gap energies results that the synthesized material was of semiconducting behavior. Calculations of Fermi energy and Urbach energy also supported semiconducting nature of the nanoparticles.

Pascu *et al.* (2012) reported about the comparison of properties of iron oxide nanoparticles synthesized by two different synthesis techniques. They synthesized iron oxide nanoparticles by non-aqueous microwave assisted sol-gel method and thermal decomposition method. They used iron (III) acetylacetonate as precursor and oleic acid as stabilizer. In case of microwave assisted method they synthesized nanoparticles of 6nm size by applying moderate temperature of 160 °C and fast reaction time of 5 minutes. They concluded that nanoparticles synthesized by microwave assisted method showed lesser surface reactivity as compared to those of synthesized by thermal decomposition. Direct stabilization of synthesized iron oxide nanoparticles in aqueous or organic media was observed in case of microwave assisted method by using either electrostatic or steric stabilizers. They reported that by using microwave-heating method highly crystalline irregular-lobular shaped nanoparticles with tremendous magnetic properties were observed. While in case of nanoparticles synthesized by thermal decomposition method monocrystalline hexagonal or spherical shaped nanoparticles were observed with a slender number of larger rectangular ones. Hence microwave synthesis method reduced the energy consumption to 40% with respect to overall cost for the synthesis of iron oxide nanoparticles.

Riaz *et al.* (2012a) experimentally investigated synthesis of Fe$_3$O$_4$ nanotubes to study various magnetic parameters like saturation magnetization and squareness. They used AAO as template for the growth of nanotubes. They observed the formation of single phase magnetite nanotubes. Uniform, large area growth of nanotubes was confirmed by SEM. They also concluded that on the basis of synthesis conditions easy axis of magnetization changed from parallel to perpendicular direction.
Bagheri et al. (2013) synthesized hematite nanoparticles by sol-gel method. They used iron nitrate as precursor and gelatin was used as polymerizing agent. The calcination of the precursor compound was performed at temperature of 600°C. They used XRD, TEM, SEM, FTIR, TGA techniques to investigate the size, shape, chemical state and thermal behavior of the nanoparticles. XRD results showed that particles size decreased while crystallinity increased by using gelatin solution. In calcined samples, FTIR spectrum revealed the presence of trivial amount of OH-groups. They reported that uniformly spherical nanoparticles were observed by SEM micrographs while TEM result showed that the morphology of the nanoparticles was pseudo spherical. The size of the nanoparticles from TEM was about 30–40 nm. Band gap energy was calculated from UV–Visible spectrum and was around 2.2 eV. They concluded that sol-gel method was cost effective, simple and environment friendly method for the synthesis of α-Fe$_2$O$_3$ nanoparticles.

Cui et al. (2013) synthesized large-scale iron oxide nanoparticles by using sol-gel method. They used FeCl$_2$.4H$_2$O as precursor and ethanol as solvent to synthesize different phases of iron oxide nanoparticles such as α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$. X-ray diffraction results revealed that the crystallite size of Fe$_3$O$_4$, γ-Fe$_2$O$_3$ and α-Fe$_2$O$_3$, calculated by using Scherrer analysis, was reported as 7.5, 8.6 and 18.4nm, respectively. Transmission electron microscopy (TEM) result showed that the synthesized nanoparticles had spherical shaped morphology. In order to distinguish between different phases they used XPS and binding energy of 708.6 eV was attributed to Fe$_3$O$_4$, while 710.8 eV was assigned to γ-Fe$_2$O$_3$. They concluded that different phases of iron oxide were obtained with variation of drying conditions.

Riaz et al. (2013a) reported about the use of presence of oxygen for the preparation of iron oxide thin films. The oxygen flow rate was varied from 5 sccm to 20 sccm which indicated the formation of mixed phases. Resistive and e-beam heating procedures were applied to get the evaporation of thin films of iron. They concluded that thin films, deposited under oxygen flow rate of 10 sccm, resulted in ferrimagnetic property with magnetization of ∼1.6 emu. When they annealed these thin films in the presence of magnetic field of 500 Oe at 350 °C strong ferrimagnetism was obtained with increase in magnetization ∼4.5 emu. They also concluded that at 250 °C transition between one phase of iron oxide to the other phase was obtained. SEM study revealed that for films deposited under 10 sccm O$_2$ flow rate, the granular structure was confirmed with grain size of 50 nm.
Silva et al. (2013) used modified sol-gel method to synthesize Fe$_2$O$_3$ nanoparticles. They used ferric nitrate (Fe(NO$_3$)$_3$•9H$_2$O) as precursor and poly vinyl alcohol (PVA) was used as solvent to obtain mixture of hematite and maghemite nanoparticles along with pure maghemite nanoparticles. They concluded that synthesized nanoparticles had sizes ranging from 15 to 53 nm and that was confirmed by XRD. Ratio of iron and poly vinyl alcohol was varied as 1:6, 1:12, 1:18, and 1:24 in order to control hematite/maghemite ratio and size of the nanoparticles. They observed that with increasing PVA amount until 1:18, maghemite content increased while average particle size decreased. Scanning electron microscope results revealed that hematite and maghemite nanoparticles showed hexagonal and cubic morphology, respectively. Maximum value of direct band gap energy of 1.91 eV was obtained for A18 sample. Superparamagnetic behavior was observed in case of field cooling and zero field cooling curves of the nanoparticles. Hematite Neel transition and maghemite to hematite phase transition was observed at 1015K and 700K, respectively. Increased magnetization was reported with increased PVA content.

Lemine et al. (2014) reported about the synthesis of iron oxide nanoparticles with sizes in the range of 14 to 30nm. They used sol-gel method. They used iron (III) acetylacetonate as precursor and methanol as solvent. They reported about the obtained maghemite phase with non-negligible coercive field giving ferro/ferromagnetic nature of iron oxide nanoparticles. In order to study their use in biomedical applications; they also calculated specific absorption rate (SAR) as a function of frequency, size and amplitude of the applied magnetic field. At 110 kHz and 190 Oe, they observed mean heating efficiency of 30 W/g for the smallest particles.

Rana et al. (2014) reported about the synthesis of magnetite nanoparticles by using co-precipitation method. They used FeCl$_3$•6H$_2$O and FeCl$_2$•4H$_2$O as precursor. Ultra-pure water and sodium hydroxide were used as solvent and precipitation agent. They synthesized two samples with pH of 10 and 12 to get nanoparticles of 10 nm and 16 nm size, respectively. Spinel phase of the synthesized nanoparticles were confirmed by XRD patterns however by Raman spectra impure phase in smaller nanoparticles with 10nm size was observed. In comparison to bulk values, they reported lower value of saturation magnetization, which was due to larger surface area of both samples. Optical band gap was also investigated with same aspect.

Riaz et al. (2014a) experimentally investigated the effect of pH on properties of iron oxide nanoparticles synthesized by modified co-precipitation method to study their magnetic properties for biomedical applications. They used FeCl$_3$•6H$_2$O and FeCl$_2$•4H$_2$O as precursors and deionized water as solvent with NaOH as a precipitation agent. They varied pH from 2-10 with increase of
The pH was varied by the addition of NaOH and magnetite nanoparticles with variation in size were obtained with variation in pH. They concluded that pure magnetite phase was confirmed from XRD results. The magnetic properties revealed that for pH 4, 6, 8 and 10 magnetite nanoparticles showed superparamagnetic behavior. They also concluded that for nanoparticles synthesized with pH 8, high value of squareness was obtained. While, they observed that particle size varied between 25 and 100 nm by SEM.

Tadic et al. (2014) reported about the synthesis of Hematite ($\alpha$-Fe$_2$O$_3$) nanoparticles. They used hydrothermal method for the synthesis. Iron sulfate heptahydrate Fe$_2$(SO$_4$)$_3$•7H$_2$O was used as precursor. They observed $\alpha$-Fe$_2$O$_3$ phase by X-ray powder diffraction (XRPD) of the sample. They reported narrow size distribution along with spherical morphology of the synthesized nanoparticles by using transmission electron microscopy (TEM). XRD and TEM revealed that the average size of hematite nanoparticle was estimated to be about 8 nm. Superconducting quantum interference device (SQUID) magnetometry was used for the measurement of magnetic properties. A divergence between zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of nanoparticles was observed below irreversibility temperature of 103 K. The maximum value of zero field cooled magnetization curve was obtained at blocking temperature of 52 K. Superparamagnetic behavior of synthesized nanoparticles was concluded with highest saturation magnetization of 3.98emu/g. Langevin function was used to obtain the fitted M(H) data to obtain the diameter and magnetic moment, which were 8.1nm and 657 B, respectively.

Guo et al. (2015) reported about the synthesis of self-assembled hematite, magnetite and maghemite flowerlike with 3 µm diameter. They synthesized nanostructures of these phases by thermal decomposition followed by simple calcination. They used ferric chloride and ethylene glycol as precursor and solvent, respectively. They studied dielectric and magnetic loss for all the synthesized nano-flowers. They concluded that magnetic loss and dielectric loss of maghemite flower are lower than those of magnetite flower. Due to presence of large saturation magnetization and crystalline anisotropy, magnetite shows enhanced microwave absorption property as compared to maghemite flowers. They also concluded that this microwave absorption of magnetite flowers is due to magnetic loss and not due to dielectric loss, while the reason for magnetic loss is natural resonance.

Macher et al. (2015) reported about the synthesis of ultrathin iron oxide nanowhiskers. They synthesized these nanowhiskers by using an iron oleate/oleylamine complex and obtained 2 × 20 nm sized iron oxide nanowhiskers after heating at 150 °C. They obtained nanostructures with
high surface to volume ratio and strong paramagnetic properties which make them suitable candidate for positive (T1) contrast agent in magnetic resonance imaging.

Yadav et al. (2015) reported about the synthesis of high-performance nanocomposite films of iron oxide/cellulose. Nanocomposite films were prepared by synthesizing iron oxide nanoparticles and their impregnation into a stimulated cellulose film. X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, thermo-gravimetric analysis were used to study structural properties and thermal stability of the nanocomposite films. They concluded that higher hydrogen-bonding interactions were observed between Fe₂O₃ nanoparticles and cellulose in FTIR. SEM results showed that size of the iron oxide nanoparticles was found to be 29 nm. TGA results proposed that the incorporation of iron oxide nanoparticles in regenerated cellulose film resulted in enhanced thermal stability to the regenerated cellulose film.

Basith et al. (2016) reported about the synthesis of iron oxide nanoparticles using sol-gel method. They investigated the effect of weight ratio of citric acid on the structural properties of nanoparticles. They used iron nitrate and water as precursor and solvent, respectively. XRD, TEM, HR-SEM, VSM and PL spectra were used to study structure, morphology, magnetic and optical properties of Fe₃O₄ nanoparticles. They concluded with the confirmation of synthesis of spherical iron oxide nanoparticles with diameter in the range of 10-18 nm. They observed room temperature ferromagnetic behavior with 20.83 emu/g saturation magnetization.

Leonardi et al. (2016) reported about the use of sol-gel and electro spinning methods to get a comparison of the various properties of synthesized Hematite nanostructures. Iron nitrate and iron acetate were used as precursors for the synthesis of hematite nanostructures in case of sol-gel and electro spinning, respectively. XRD, Raman, SEM and TEM were used to investigate structural, morphological properties. They concluded that by using sol-gel method hematite nanoparticles were synthesized while fibrous nanostructures comprising of interconnected particles were obtained by using electro-spinning technique. The synthesized nanostructures were then utilized in gas sensor fabrication. They hypothesized that different sample textures affected sensing performances for ethanol detection.

Mirzaei et al. (2016) reported about the synthesis of hematite nanoparticles. They used Pechini sol–gel method with annealing of 550 °C for 3 hours. They used iron nitrate and distilled water as precursor and solvent, respectively. Ethylene glycol was used as esterification agent. XRD, Raman analysis, XPS and SEM was used to investigate structural and morphological properties of the synthesized hematite nanoparticles. They also investigated electrical and sensing properties
of synthesized nanoparticles. They concluded that hematite based sensors produced improved selectivity and sensibility towards ethanol at 225 °C.

3.3 Theoretical Investigations of Iron oxide Nanostructures

Ermakov et al. (2013) reported about the theoretical investigation of the electronic structure and geometry of magnetite (Fe₃O₄) cluster. They used semi-empirical PM6 method while dealing with density functional theory. They obtained consistent data for cluster geometry by using different methods while did not get the identical results for geometry optimization by different methods. They predicted the presence of two states i.e. high spin and low spin ones with similar stability. They correlated experimentally determined properties of magnetite thin films and nanomagnetite with theoretically calculated magnetic properties, vibrational spectra and stimulated geometry. They concluded that Fe–Fe and Fe–O bond lengths in magnetite cluster were smaller than bond lengths in bulk magnetite. The average energy estimated for Fe-O was 250 KJmol⁻¹.

Gillen and Robertson (2013) investigated the density of states and band structures of FeO. They used hybrid density functional with screened exchange local density approximation (sX-LDA). That approximation was implemented in CASTEP, which is the code for plane wave. The transition metal oxide FeO was modeled by a rhombohedral unit cell comprising two oxygen atoms and two metal atoms. In order to get convergence antiferromagnetic spin ordering was used for all calculations along the crystal direction of [111]. That antiferromagnetic spin ordering revealed lowest total energy for the system. They used lattice constant of 8.53 Å and bulk moduli of 207.66 GPa. Pseudo-potential was generated by using OPIUM code for Fe. 3d, 4s and 4p states of the transition metal were treated as valence electrons. The cutoff energy for these valence electrons was 750 eV. Density of states plots were calculated by using 12×12×12 grid of k-points. They compared their results with existing experimental data and showed that their calculations largely yielded precise calculations for the valence bands and fundamental band gaps. They concluded that energy difference was 1.1 eV approximately between the single d band and top of the valence band of bulk FeO. They reported the indirect band gap of 2.45 eV.

Wdowik et al. (2013) investigated the effect of cation vacancies on vibrational and electronic properties of the wüstite. They used VASP code with generalized gradient approximation with on-site coulomb potential of 6 eV to calculate electronic properties of wüstite. They used super cell of 74 atoms to calculate the lowest energy, required to get stable structure. Two different sets
of structures with the removal of one or two iron atoms were used. They investigated the density of states and observed splitting of crystal field symmetry. They concluded that insulating gap was 50% reduced because of unoccupied electronic bands presented by Fe$^{3+}$ ions, which were stabilized by cation vacancies. They suggested that in wüstite strong electron-phonon coupling was present.

Noh et al. (2014) reported the investigation of electronic, structural and magnetic properties by using density functional theory. They used different exchange correlation potentials like GGA and GGA+U, HSE (15%) and HSE06. They used Vienna ab-initio as Simulation Package with cubic phase of magnetite in Fd3m space group. They used PBE as exchange correlation potential for GGA and GGA+U with 4 eV as effective value of U in case of GGA+U calculation. They concluded that structural relaxation with functionals like PBE and PBE+U show slightly varied lattice constant. Half metallic behavior was observed in case of HSE06 functional. They observed that PBE+U gave best results as compared to other hybrid functional.

Wanaguru et al. (2016) reported about the use of density functional theory to investigate electronic, geometric and magnetic properties of $\alpha$-Fe$_2$O$_3$ nano-ribbons. Vienna ab initio simulation package with PBE (Perdew–Burke–Enzerhof) functional in generalized gradient approximation was used. In case of GGA+U they used 4 eV as the effective value of Hubbard potential while 400 eV was the cut off energy used for all calculations. They generated nano-ribbons by atomically cutting thin hematite nano-sheets along [010] and [100] directions. They observed tunable semiconducting behavior for nano-ribbons from (110) surfaces. They concluded that ending nature, showing pseudo-Jahn-Teller effect, was obtained in case of nano-ribbons generated from (104) surface. For other type of nano ribbons they observed preserved stoichiometry with built-in oxygen vacancy. Half metallic behavior at larger width of these nano ribbons was also obtained due to built-in oxygen vacancy. They reported 1.66 eV and 1.79 eV value of band gap for (110) surfaces based hematite nano-ribbons.

Zhou et al. (2016) investigated the effect of different density potentials applied to investigate structural and electronic properties of bulk hematite by using density functional theory. VASP code with spin polarization was used. They used DFT and DFT+U methods for different functionals (LSDA, PBE, PBEsol–HSE06, PBE–HSE-12%, HF and PBE–HSE06). In case of DFT+U calculations Hubbard potential of 5 eV was used. By using these potentials they calculated cohesive and formation energy. They used ionic nature of hematite to investigate magnetic moment, band gap and hybridization of 2p and 3d states of oxygen and iron,
respectively. They concluded that electronic properties were improved by using PBE+U and LSDA+U potentials while all other properties got improved by using hybrid functionals.

### 3.4 Investigations on Iron Oxide Based Nanostructures

In literature, Beltran et al. (2013) reported about effect of Fe, Co and co-doping of these two transition elements in order to study the origin of magnetic nature in Fe: Co co-doped ZnO nanoparticles. They varied $x=0$ and 0.05 for both Fe and Co in basic formula for transition metal doped ZnO i.e. Zn$_{1-x}$M$_x$O while in case of co-doping Zn$_{0.90}$Fe$_{0.05}$Co$_{0.05}$O was used. Sol-gel method was used for the synthesis of nano-powders. From XRD analysis they concluded that in place of Zn$^{2+}$ ions substitution of Co$^{2+}$ ions took place on tetrahedral sites. Mössbauer spectroscopy of Fe showed that Fe$^{3+}$ ions were present in case of Fe and Fe+Co co-doping. They obtained small traces of ZnFe$_2$O$_4$ in Zn$_{0.95}$Fe$_{0.05}$O, while in case of Zn$_{0.90}$Fe$_{0.05}$Co$_{0.05}$O no such impurity was detected. They also concluded that the co-doping of Fe and Co in ZnO showed impurity free results with strong charge transfer ferromagnetic properties due to involved mixed valence ions in co-doped samples.

Kumar et al. (2014) synthesized Zn$_{1-x}$Fe$_x$O with $x$ greater or equal to 0.000001 and smaller or equal to 0.1. They used co-precipitation method along with annealing for the synthesis of nanocrystalline powders. They concluded that hexagonal wurtzite ZnO crystal structure was confirmed by XRD and average crystalline size of 8nm to 15 nm of the synthesized samples were obtained from TEM analysis. FTIR results confirmed the incorporation of iron ions in ZnO lattice. They reported about improved photocatalytic performance in case of iron doping as compared to those for un-doped ZnO. They performed room temperature magnetic measurements which showed diamagnetic behavior of un-doped ZnO while in case of minute iron doping ferromagnetic behavior was observed. On the other hand they also obtained paramagnetic behavior for the samples with 10% iron doping.

Ciciliati et al. (2015) reported about the synthesis of Fe doped ZnO nanoparticles. They used zinc nitrate (Zn(NO$_3$)$_2$•6H$_2$O and iron nitrate (Fe(NO$_3$)$_3$•9H$_2$O) as precursors and water as solvent in sol-gel method for the synthesis process. They investigated structural properties using XRD which resulted wurtzite structure of samples. The phase purity was disturbed when doping of iron was increased to 2 mol% and hematite traces were obtained. Optical properties were investigated by UV–Vis which showed decreased band gap of 2.3 eV for doped nanoparticles while un-doped ZnO showed highest value of band gap i.e. 3.1 eV. Confirmation of hexagonal nanoparticles with
increased surface area was also confirmed by TEM results. Surface area was increased from 18 nm to 55 m²g⁻¹.

Kanchana *et al.* (2016) reported the synthesis of iron-doped ZnO nanoparticles using chemical precipitation technique. They investigated compositional, structural and optical properties by XRD, SEM, TEM and UV-spectrophotometer. Polycrystalline samples with wurtzite structure were confirmed by XRD. XRD also confirmed that crystallites were in the range of nanometer size, which increased from 25-36 nm by increasing doping concentration. The nanometer size confirmation was also done by SEM results. Occurrence of stretching bonds was further confirmed in Zn–Fe–O by FTIR results. Red shift in doped samples was also obtained from UV-spectrum. The increased doping concentration from 0-6% showed decrease in band gap energy from 3.30-3.23 eV.

Sharma *et al.* (2017) studied structural, magnetic and optical properties of ZnO nanoparticles (un-doped and Fe/Co co-doped). They used co-precipitation method for the synthesis of nanoparticles. For the investigations of above said properties they used XRD, FTIR, TEM, SEM, VSM, PL spectroscopy and UV–Vis. They concluded that for both un-doped and co-doped samples they obtained hexagonal wurtzite pure single phase crystal structure. Same results were also confirmed by FTIR due to the presence of tetrahedral coordination. Surface morphology was also confirmed by SEM and TEM and revealed that well defined grains were formed for synthesized samples. They also concluded that possible reason for room temperature ferromagnetism in co-doped samples was because of presence of oxygen vacancies and grain boundaries. Optical properties with decrease in band gap from 3.20 eV 2.41 eV were also reported along with PL spectra which demonstrated the presence of five peaks in visible spectra.

### 3.5 Summary

After getting the analysis of various experimental techniques for the synthesis of iron oxide nanostructures, we have come to the conclusion that either these methods use high cost materials or they use high synthesis temperature with high cost apparatus. All these parameters make these synthesis techniques unfavorable for being used. Also use of expensive precursors, stabilizing agent/surfactant and organic solvents increase the overall cost of the reaction. In conclusion, we require a low cost, low temperature and simple method, which yields nanostructures with controlled morphologies and phases. So we used sol gel method. Although some researchers used sol-gel method but calcined as synthesized samples at high temperature or used high synthesis
temperature to get desired phase. So our motive was to work by using low temperature sol-gel method to get nanostructures of pure phase iron oxide with low synthesis cost.

On the other hand, after the literature review about theoretical calculations done by various researchers, it was observed that they used different codes with different parameters to investigate the structural, electronic and optical properties. While dealing with density functional theory with Hubbard potential, most of them use larger value of Hubbard potential (U eV) to get improved optical properties. But to the best of our knowledge there are no such reports of structural, electronic and optical properties of different iron oxide phases with such a low value of Hubbard potential. Also it is required to investigate the role of iron and oxygen individually. Hence, from these findings we used density functional theory with low values of Hubbard potential to get repeatable improved results.

In case of iron oxide based nanostructures ZnO, being the material of interest due to its wide band gap, was selected as host material. Many researchers showed its diamagnetic nature at room temperature. In current century main focus of researchers is in new materials with wide band gap and improved magnetic properties so for that purpose doping of various transition metals in ZnO was done. After analyzing all these requirements we selected Fe and Mn in our case for separate and co-doping of these transition metals in ZnO experimentally and theoretically.
CHAPTER-4
Chapter – 4

Experimental Details

4.1 Introduction

Several methods have been stated to synthesize iron oxide nanoparticles. Most of them are through the conventional top-down approach, in which big objects are modified into small ones (Vashist et al. 2012). On the other side some synthesis methods follow bottom-up approach, which is a chemical approach and it synthesizes nanostructures by arranging atom-to-atom or molecule-to-molecule. Bottom-up approach is most beneficial for the synthesis of uniform sized nanoparticles as compared to the top-down approach as in top-down approach it is difficult to control size and shape of the nanoparticles. Previously frequent physical methods have been used to synthesize nanoparticles, such as melt spinning (Mertens et al. 2015), laser ablation (De Bonis et al. 2015), mechanical ball milling (Fathinia et al. 2015) and vacuum-deposition (Cannas et al. 2011). By using these methods large quantity of highly pure magnetic nanoparticles can be produced. But, they mostly have slight control on structural morphology, size of the nanoparticles and on their distribution (Ling and Hyeon 2013).

Chemical routes for the synthesis of nanostructures represent a type of bottom-up approach, which utilizes chemical methods to initiate and control the assembly process of the atomic or molecular building blocks. Though there has not been a general method applicable to the synthesis of all kinds of nanostructures. A variety of these chemical or bottom-up pathways include thermal decomposition (Hufschmid et al. 2015), microemulsion methods (Okoli et al. 2012), sol-gel (Cui et al. 2013) and metal salt co-precipitation (Cannas et al. 2011; Ling and Hyeon 2013).

Synthesis technique along with different parameters and conditions are responsible for the structural and magnetic properties of the resultant product (Vesel and Balat-Pichelin 2014). It has always been a challenge for researchers to produce size controlled and pure shaped, qualitative and quantitative nanostructures by using environment friendly and economical routes. Structural properties and morphology of the substrate also play an important role in determining these properties (Vesel and Balat-Pichelin 2014). In the last few decades, there is a tremendous development in the field of nanotechnology. One of the reasons of this development is the advancement in characterization techniques.
In this chapter, techniques and processes involved in the synthesis of iron oxide based nanostructures are presented. This chapter also includes the techniques to characterize the resultant nanostructures.

4.2 Synthesis Approaches

There are different ways for classification of synthesis routes of various nanostructures. One is based on the initial state of material, namely solid, liquid and gas (Murty et al. 2013). Generally, synthetic methods of nanostructures are classified into two approaches that are Bottom-up approach and Top-down approach (Silva 2004; Vashist et al. 2012).

4.2.1 Top-Down Approach

In the top-down approach nano-machining of materials at macroscopic level is performed below the preferred nanometer scale by using isotropic (chemical) or anisotropic (physical) processes (Vashist et al. 2012). Electron beam lithography, mechanical alloying, laser ablation, ion and plasma etching, photolithography and anodization are some important techniques following top-down approach (Murty et al. 2013).

Best example of the top-down approach is the most famous lithography technique (Silva 2004; Vashist et al. 2012). Hence, in top-down approach, synthetic techniques initiate with material at macroscopic level and results in nanostructures (Silva 2004).

4.2.2 Bottom-Up Approach

Bottom-up approach involves the formation of material at nano-level, starting from molecular or atomic components. Larger entities are not used at the starting point to get accumulation of material (Vashist et al. 2012). Hence, during this approach, synthesis techniques start by synthesizing small custom-made molecules. These molecules have the capability to self-assemble and form nanostructures (Silva 2004). “Bottom-Up” approach became the innovative and revolutionized approach, in the world of nanotechnology, to synthesize numerous nano-materials (Vashist et al. 2012).

The main challenge of this approach is the synthesis of such molecules that spontaneously self-assemble when controlled change occurs such as change concentration of solute, change in pH, or by changing the applied electric field (Silva 2004). Physical vapor deposition, chemical vapor
deposition, chemical precipitation, spraying synthesis and sol-gel process are some of the techniques following bottom-up approach (Murty et al. 2013; Silva et al. 2013).

Generally, techniques following bottom up approach result in very fine nanostructures such as individual nano-shells or individual nanoparticles. Narrow size distribution of these nanostructures is obtained by controlling the synthesis parameters. While, techniques following top down approach usually do not result in individual nanostructures; although they can yield bulk nanostructures (Murty et al. 2013). Among these techniques some brief description of sol-gel method is given here in next Section 4.3.

**4.3 Sol-Gel Technique**

Sol-gel is a wet chemical method. A state in which colloidal particles forms stable suspension within a liquid is called sol while gel can be defined as three dimensional, porous solid network surrounded by continuous liquid phase (Brinker et al. 1996; Pierre 2013). Hence sol-gel process comprises the generation of a sol (colloidal suspension), which is consequently changed to gel and solid material (Murty et al. 2013).

Starting from reactive metal precursors, sol-gel process takes place in three main reaction steps; initially hydrolysis which is followed by condensation and last step of sol-gel process is polymerization. In hydrolysis, alkoxy group i.e. OR of metal alkoxide (M-O-R) is replaced by hydroxo ligand i.e. (OH) as given in Equation (4.1).

\[
M-O-R + H_2O \rightarrow M-OH+R-OH \quad (4.1)
\]

Where metal alkoxide is metal-organic compound in which metal is attached to organic ligand. Nature of alkyl group and solvent, temperature, concentration of the precursor, molar ratio of alkoxide and water and presence of catalysts (acidic or basic) are various factors which affect the hydrolysis in sol-gel process (Murty et al. 2013).

Metal oxides are produced by subsequent condensation which eliminates either alcohol or water (Murty et al. 2013). Oxolation and olation are the two main reactions occuring in condensation as given in Equation (4.2 (a) and (b)), respectively. In oxolation two metal cations are attached by ‘oxo’ bridge such as M-O-M while in olation reaction the connecting bridge of two metal cations is ‘OH’ instead of ‘O’.

\[
\begin{align*}
M-OH + HO-M & \rightarrow M-O-M + H_2O \quad (4.2a) \\
M-OH +M-OH_2 & \rightarrow M-OH-M + H_2O \quad (4.2b)
\end{align*}
\]
The last step is polymerization, which is occurred in three stages. In the first stage polymerization of the monomer units is observed. Growth of the particles is the second phase of polymerization. In the third stage formation of gel is obtained due to the linkage of particles into chains and then in solid networks (Murty et al. 2013). Amorphous or crystalline coating is obtained due to further heat treatment which pyrolysis remaining organic or inorganic components (Brinker et al. 1996).

Sol-to-gel transition permits the solid phase to be formed into fibers, films or microspheres (Brinker et al. 1996). Hence, different products can be obtained, with the variation in different conditions. Comprehensive explanation of the process and the products obtained is given in Figure 4.1.

![Flow diagram of sol-gel process](image)

**Figure 4.1: Flow diagram of sol-gel process (Righini and Chiappini 2014).**

This technique is widely used in material sciences and ceramic engineering. Final products are attained with preferred properties like tailored porosity, optical transparency, thermal resistance and chemical durability (Olding et al. 2001).

### 4.3.1 Advantages of Sol-Gel Process

Sol-gel method has diverse advantages over other synthesis techniques to get nanostructures such as metal oxide nanoparticles (Murty et al. 2013). These include the synthesis of nanostructures with high purity due to multiple distillations of the products during the process (Riaz 2008).
Large-scale production of these nanostructures on industrial level is also one of the advantages of sol-gel method. Sol-gel process provides a degree of control of structure and composition at molecular level (Murty et al. 2013).

By using sol-gel method, chemical composition of the final product can be controlled at low cost and low temperature (Basith et al. 2016). By controlling different parameters, such as temperature, pH time of reaction and concentration, materials can be shaped easily into complex geometries. In short, it is a simple, economic and effective method for the production of nanostructures (Riaz 2008).

4.4 Characterization

Characterization of nanostructures has been mostly based on certain critical improvement in conventional tools and methods used for the characterization of bulk materials (Murty et al. 2012). The synthesized and fabricated nanostructures were characterized by using Bruker D8 Advance Diffractometer, Hitachi S-3400N Scanning Electron Microscope, Renishaw inVia Raman Spectroscope, LCR meter Quadic 1920 meter, J.A. Woollam Spectroscopic Ellipsometer and Lakeshore 7404 Vibrating Sample Magnetometer. Details of the characterization techniques are given below.

4.4.1 X-Ray Diffractometer (XRD)

X-ray diffraction has been extensively used to find crystal structure, crystalline character, lattice constants and crystallite size of various nanostructures such as thin films, nanowires and nanoparticles. X-Ray diffractometer (XRD) is a non-destructive, powerful and versatile technique that tells detailed information about the crystallographic structure and chemical composition of natural and synthetic materials (Murty et al. 2013). This technique helps to distinguish between single phase, multiphase crystallite and amorphous materials. In XRD technique, data interpretation is straight forward and simple with negligible requirement of sample preparation (Murty et al. 2013).

4.4.1.1 Bruker D8 Advance Diffractometer

Bruker D8 Advance Diffractometer, as shown in Figure 4.2, was used for structural characterization of the synthesized samples. CuKα radiations were used as an X-ray source whose wavelength is $\lambda=1.5406\text{Å}$. Copper and Nickel are used as target and filter, respectively.
4.4.2 Scanning Electron Microscope (SEM)

Scanning electron microscope is one of the commonly used techniques to characterize nanostructures and nanomaterials (Murty et al. 2013). Numerous types of signals are produced by SEM, such as secondary electrons, Auger electrons, back scattered electrons, characteristic X-Rays, Photons with different energies and specimen current (Goldstein et al. 2012), as shown in Figure 4.3.

Scanning electron microscope is a powerful instrument which permits the characterization of heterogeneous inorganic and organic materials and nanostructures by scanning the surface and gives images (Goldstein et al. 2012).
SEM can be efficiently used to characterize samples below the resolution of only a few nanometers, while the image magnifications can be achieved in the range of approximately ten to over three hundred thousand (Murty et al. 2013). Besides giving the information about surface topography and morphology of the sample, SEM can also give valuable information on crystal orientation, internal stress distribution and composition of the prepared sample (Goldstein et al. 2012).

4.4.2.1 Hitachi S-3400N SEM

We used Hitachi S-3400N Scanning Electron Microscope (SEM) for investigation of the surface morphology of the synthesized nanostructures, as shown in Figure 4.4. Accelerating voltage in the range from 0.3 to 30 V can be applied while 6-270 Pa is the range for low vacuum for its operation. 4 nm and 3 nm is the value of resolution in case of back scattered electron image resolution and secondary electron image resolution, respectively. Besides its all operational advantages it is a user friendly scanning electron microscope which gives high performance.

Figure 4.4: Hitachi S-3400N Scanning electron microscope.

4.4.3 Vibrating Sample Magnetometer (VSM)

Vibrating sample magnetometer (VSM) is a scientific instrument which is used to measure magnetic properties of the synthesized materials. The first vibrating sample magnetometer was invented by Simon Foner in 1959 (Foner 1959). Magnetic properties of the material can be calculated by applying magnetic field to the samples (Kulkarni 2015).
4.4.3.1 Lakeshore 7407 VSM

Magnetic properties of the synthesized nanostructures were studied by using Lakeshore 7407 VSM shown in Figure 4.5, at room temperature.

![Figure 4.5: Lakeshore 7407 VSM.](image)

By using Lakeshore 7407 VSM various parameters such as hysteresis loops, saturation magnetization, retentivity, coercivity, slope at Hc, squareness ratio, DC and AC remanence, switching field distribution and time dependent magnetization data can be measured directly or can be derived by software (Riaz 2008).

4.4.4 Impedance Analyzer

An impedance analyzer can be defined as “a computational device that measures opposition to current in alternating current (AC) systems”. As compared to other characterization techniques it is a new technique which is more powerful as well. The impedance analyzer spectroscopy is used to investigate the electrical properties. Relaxation frequency of sample can also be determined using this spectroscopic technique. This frequency is always independent to geometrical shape of sample (Barsoukov and Macdonald 2005).

4.4.4.1 Analysis using Impedance Analyzer

By using Impedance Analyzer dielectric constant can be calculated by Equation (4.3).

\[
\varepsilon' = \frac{C_d}{\varepsilon_o A} \quad (4.3)
\]

In the above formula, C is the capacitance of the nanostructure measured in farads, ‘d’ is the thickness in meters, ‘A’ is the cross-sectional area of the flat surface of the thin film and ‘\(\varepsilon_o\)’ is
the constant of permittivity of the free space. The formula to calculate tangent of the dielectric loss angle is as given in Equation (4.4).

\[
\text{Tan}\delta = \frac{1}{2\pi f R p C p} \quad (4.4)
\]

In the above formula ‘δ’ is the loss angle, ‘f’ is frequency, R is resistance and C is the capacitance. Dielectric loss factor in terms of tangent loss factor is defined in Equation (4.5).

\[
\varepsilon'' = \varepsilon'Tan\delta \quad (4.5)
\]

The basic approach of impedance spectroscopy is to provide a small but detectable sinusoidal pulse to the prepared sample under consideration and to determine its response (current or voltage or another signal of interest). The electrical parameters are determined using impedance spectroscopy i.e. the determination of impedance as a function of frequency. This technique finds its applications very rapidly in the electrical characterization of heterogeneous structures (Barsoukov and Macdonald 2005; El Hiti 1999).

### 4.4.4.2 6500B Impedance Analyzer

Precision Impedance Analyzer 6500B, as shown in Figure 4.6, was used for the dielectric measurements. This provides a very precise and fast testing of the components at different ranges of frequencies up to 20 MHz. It has high measurement accuracy of about ±0.05% making the instrument the best fit for the purpose. Basic accuracy for capacitance, inductance and impedance is ±0.05%. Accuracy for dissipation factor is ±0.0005%. We also connect external monitor or projector to the instrument.

![Figure 4.6: 6500B Impedance Analyzer.](image)

### 4.4.5. Raman Spectroscopy

In 1928, Raman and Krishnan discovered this phenomenon of Raman spectroscopy for the first time (Raman and Krishnan 1928). It is a powerful technique to investigate structural properties of materials as variation in particle size can also be measured by using Raman spectroscopy (Shinde
et al. 2011). It is a fast tool used to distinguish different phases of materials such as oxides, oxyhydroxides and hydroxides of iron. It is also used in the investigation of the pigments in historical artwork and of archaeological material. Investigation of bio mineralized material and mineral composition of meteorites can also be studied by using this characterization technique (Hanesch 2009).

Hence, Raman spectroscopy of various samples in different physical states can be performed like vapors, liquids, solids, in bulk form, in cold and hot states, as surface layers or as microscopic particles (Paudel et al. 2015; Smith and Dent 2013).

4.4.5.1 Basic Principle of Raman Spectroscopy
Basic principle of Raman spectroscopy is the Raman Effect. It is a scattering technique, in which inelastic scattering of electromagnetic radiation by sample take place (Ferraro 2003). Crystal lattice of sample has vibrational modes known as phonons which interact with laser (monochromatic light). Shifting of the energy of scattered light occurred due to scattering. As a result of this shifting of energy, a spectrum appears known as Raman spectrum. There is a specific spectrum for each mineral due to the presence of specific phonons for each corresponding mineral (Hanesch 2009).

4.4.5.2 Working and Operation of Raman Spectroscopy
Laser, wavelength analyzer, collection optics, computer, detector and filter (for laser rejection known as notch filter) are the main components of the Raman spectrometer, as shown in Figure 4.7(McCreery 2005; Paudel et al. 2015).

In Raman spectroscopy, monochromatic laser is used to illuminate the sample. This laser beam interacts with molecules of materials and as a result of this interaction scattered light is originated. This process of scattering is inelastic as scattered light have different frequency from that of incident light. This difference in frequencies constructs a Raman spectrum.

Hence, inelastic collision between molecules of material and incident monochromatic radiation is the main reason of Raman spectra (Paudel et al. 2015). There is no requirement of sample preparation in case of Raman spectroscopy (De Faria et al. 1997). Choice of laser wavelength is important factor while using Raman spectroscopy as it measures the frequency shift (McCreery 2005).
4.4.5.3 Renishaw inVia Raman Spectroscope

Renishaw inVia Raman spectroscope, as shown in Figure 4.8, was used to study Raman spectrum of synthesized nanostructures at room temperature.

Time and temperature varied Raman spectrum can be obtained by using Renishaw inVia Raman spectroscope. Volume scan and line scan i.e. along the surface and in depth can also be performed. It gives the detection of weak signals with quick data processing hence high resolution and good quality spectra with repeatable results can be obtained (Lu et al. 2014).

4.4.6 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy is a type of spectroscopy which used infrared spectrometer. Analysis of infrared spectrum reveals that which molecules are present in sample along with their concentration (Smith 2011). This information makes infrared spectroscopy an important tool for researchers. Infrared spectroscopy is one of the spectroscopy techniques that uses infrared region in electromagnetic spectrum. That region is defined as light with lower
frequency and longer wavelength as compared to visible light. By using all these techniques in spectroscopy one can study and identify all chemicals (Yadav et al. 2015). Different types of samples can be used in infrared spectroscopy such as solid, liquid and gaseous samples. The main instrument to produce infrared spectrum in infrared spectroscopy is called infrared spectrometer. In typical IR spectrum there is presence of transmittance or infrared light absorbance on (vertical) y-axis and wavelength or frequency on (horizontal) x-axis. Units of frequency in IR spectra are per centimeters. These are sometimes called as wave numbers having symbol cm$^{-1}$. Units of wavelength used are usually given as in micrometers with symbol μm. This unit is related to wave numbers in indirect way (Suart 2004).

There are three different portions of infrared region in electromagnetic spectrum. First one is near infrared; second one is mid infrared and last one is far-infrared. This classification is done on the basis of their distance from visible region (Smith 2011).

### 4.4.7 Spectroscopic Ellipsometry

Ellipsometry is an optical technique that characterizes the transmission or reflection of light from samples. Elliptical path of polarized light gives its name i.e. ‘ellipsometry’ with main feature like measurement of the alteration in polarized light upon transmission of light on sample or upon reflection of light on sample (Fujiwara 2007). It is widely used for the characterization of the optical substrates, thin films and multilayered structures (Losurdo and Hingerl 2013). Spectroscopic Ellipsometry is highly recommended to be used due to its fast and nondestructive measurements with high precision. Due to its real time monitoring it has wide application area (Fujiwara 2007).

#### 4.4.7.1 Instrumentation of Ellipsometer

Light source, linear polarizer, retarder, sample, linear polarizer and detector are the main parts of ellipsometer as shown in Figure 4.9.

![Figure 4.9: Main parts of Ellipsometer.](Image)
### 4.4.7.2 Calculations

Basically optical constants in ellipsometry describe the interaction of light with a material. Equation (4.6) shows refractive index as:

\[
\bar{n} = n + iK
\]  
(4.6)

Where \(n\) is the real part of refractive index and can be calculated by simple relation given in Equation (4.7).

\[
v = \frac{c}{n}
\]  
(4.7)

Where, “c” is velocity in vacuum while “v” defines phase velocity of light. In Equation (4.5) “k” is called extinction coefficient which provides information regarding the decrease in wave amplitude (Talebian et al. 2013). This extension coefficient “k” given in Equation (4.8) is in direct relationship with absorption of light and is linked with the absorption coefficient as well:

\[
\alpha = \frac{4\pi K}{\lambda}
\]  
(4.8)

Where, \(\alpha\) represents absorption coefficient and \(\lambda\) is wavelength of light.

A light beam falls on sample at some incidence angle \(\theta_i\). From that light some light is reflected at reflection angle \(\theta_r\). This reflection takes place at the boundary of medium boundary and remaining part of light is transmitted by sample at an angle of \(\theta_t\). The incidence plane contains incident, reflected as well as transmitted beams. Figure 4.10 shows incidence plane along with incident, reflected and transmitted light (Roy et al. 2013).

![Incident reflected and transmitted light](image)

**Figure 4.10:** Incident reflected and transmitted light.

Equations (4.9) and (4.10) show the relationship for calculation of transmittance “T” and reflection “R” (Nair et al. 2011).
\[ T = \frac{I_t}{I_i} \quad (4.9) \]

and

\[ R = \frac{I_r}{I_i} \quad (4.10) \]

### 4.4.7.4 J.A. Woollam Ellipsometer

J.A. Woollam M-2000 ellipsometer given in Figure 4.11 was used in our case for characterization of synthesized samples of iron oxide nanoparticles.

![J.A. Woollam M-2000 ellipsometer](image)

**Figure 4.11: J. A. Woollam M-2000 ellipsometer**
CHAPTER-5
Chapter – 5 Effects of Variation in Sol Concentration

5.1 Introduction

Iron oxide being a half metal and exhibiting ferromagnetic to anti-ferromagnetic properties with the change in iron and oxygen content is a potential candidate for use in the magnetic tunnel junctions (MTJs). New challenges and opportunities in miniaturized electronic and spintronic devices have changed the world over the last two decades. This has led to a new and exciting branch of nanoelectronics where scaling down the electronic devices to much smaller dimensions is a potential target. Spintronics exploiting the spin of electron in addition to its charge has opened a new path. For device functionality, the phenomenon, such as spin scattering and tunneling through thin films, at practical temperatures has resulted in rapid development in storage and memory devices.

Several different methods have been used to prepare iron oxide nanostructures, including sputtering, molecular beam epitaxy, and pulsed laser deposition (Hari Babu et al. 2013b; Riaz et al. 2013a; Wu et al. 2012b). However, very little attention has been devoted to use of wet chemical methods especially sol-gel.

5.2 Iron oxide Nanostructures with Variation in Sol Concentration

We here report the preparation of iron oxide nanostructures using sol-gel method. Seven different sols were prepared with variation in concentration of sol from 1.8 to 0.6 mM. It is seen conclusively that changes in sol concentration has a tremendous effect on phase purity and stability of magnetite nanostructures along with excellent ferrimagnetic properties.

5.3 Experimental Details

In this thesis, iron oxide nanostructures were prepared using sol-gel method with variation in concentration of sol from 1.8 to 0.6 mM. Two solutions were prepared before the final sol was synthesized. A 2.1 g of FeCl₃·6H₂O was dissolved in 12 ml DI water. The solution was stirred at room temperature. 18 ml n-hexane was added to the above solution that results in the presence of two distinguishable layers. NaOH and 20 ml ethanol was added to the above solution. The solution was then heated on a hot plate at 50 °C for 6 h. The heating resulted in single layered iron oxide sol. Oleic acid was added to iron oxide sol drop-wise while under constant stirring at 50°C. The sol was aged at room temperature for 48 h before the films were deposited.
Films were deposited onto copper substrates, which were firstly etched with diluted HCl and rinsed repeatedly with deionized water followed by ultrasonication in acetone and isopropyl alcohol (Riaz and Naseem 2007). Films were annealed in vacuum for 60 min and 120 min under 500 Oe applied magnetic field. Structural properties were studied using Rigaku D-MAX/IIA X-ray Diffractometer (XRD). Lakeshore’s 7407 vibrating sample magnetometer (VSM) was used to study room temperature magnetic properties. Hitachi S-3400N scanning electron microscope (SEM) was used to study the surface morphology.

5.4 Results and Discussion

One of the more remarkable features of iron oxide is its color that depends on the composition, varying from black to red and yellow (Schwertmann and Cornell 2008). This feature of iron oxide is used as a thumb rule to identify the phases by researchers (Andrade et al. 2012). In this research work, all of the iron oxide sols were black in color with little shade of red and brown suggesting the formation of magnetite along with maghemite. However, sol with molar concentration of 1.4 mM was typically black in color suggestive of formation of pure magnetite phase. The magnetic properties of various iron oxide sols were tested using VSM and our optimized sol showed super paramagnetic behavior, which indicates that the domains were already fully developed within the sol itself. Therefore, this sol was then selected for further variation during synthesis (Riaz et al. 2013a). Figure 5.1 shows X-ray diffractographs of Fe₃O₄ films prepared using sols of different concentrations (0.6–1.8 mM). Peaks corresponding to copper substrate were eliminated from the patterns. All the main peaks correspond to Fe₃O₄ phase (JCPDS card no. 72-2303). The extraneous peaks particularly with 2θ° range of 40°–50° are indexed as γ-Fe₂O₃ (JCPDS card no. 39-1346). It can be seen that the sol synthesis and annealing conditions have a strong impact on crystallinity and phase stability of nanostructures. Single phase (magnetite Fe₃O₄) is achieved only using sol with concentration of 1.4 mM. The insets of Figure 6.1(a)–(g) show diffraction patterns in the range of 5°–20°.
Figure 5.1: XRD patterns of films deposited using sol concentration of (a) 1.8, (b) 1.6, (c) 1.4, (d) 1.2, (e) 1, (f) 0.8, and (g) 0.6 mM; i) As-deposited, ii) 60 min, and iii) 120 min annealed at 300 °C (*Fe$_3$O$_4$; γ-Fe$_2$O$_3$).

Presence of diffraction peaks corresponding to maghemite phase appear in 2θ° = 5°–20°. However, no diffraction peaks corresponding to maghemite phase appear in this diffraction angle range for films deposited using molar concentration of 1.4 mM [inset of Figure 5.1(c)]. These results show that concentration of sol strongly affects the rate of reactions (along with hydrolysis and condensation) taking place in the sol, which leads to variation in the ratio of Fe$^{2+}$ cations to Fe$^{3+}$ cations (Karaagac et al. 2010). This is the reason for incorporation of γ-Fe$_2$O$_3$ in the dominant Fe$_3$O$_4$ phase. In addition, oxidation of magnetite to maghemite occurs through the outward diffusion of iron cations and inward diffusion of oxygen anions. At the surface, iron ions react with oxygen and form a thin layer of maghemite thus leading to the formation of non-stoichiometric phases. Conversion of Fe$_3$O$_4$ to γ-Fe$_2$O$_3$ involves reduction in number of iron atoms per unit cell thus preserving the inverse spinel structure. Therefore, the oxygen arrangement does not change (Tang et al. 2003). Moreover, oxygen anion is twice as large as iron cation so iron diffusion is much easier as compared with oxygen diffusion. Upon annealing the peak intensities corresponding to Fe$_3$O$_4$ phase increase, thus indicating improvement in crystallinity. However, annealing did not help in achieving a single phase in our case nor did it lead to any conversion from Fe$_3$O$_4$ to γ-Fe$_2$O$_3$. It only strengthens the phases that were already present in the as-deposited conditions. Decreasing the sol concentration to 1.4 mM improves the
crystallinity of films as indicated by increase in peak intensities corresponding to Fe$_3$O$_4$. The crystallinity of the films can be seen as a function of sol concentration in Figure 5.2(a).

Further decrease in concentration of sol causes a reduction in peak intensities. High contribution from $\gamma$-Fe$_2$O$_3$ is also observed in lower concentration films. As the main difference in Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ is the absence of Fe$^{2+}$ cations on the octahedral sites, it is reasonable that lower sol concentration corresponds to more vacancies of Fe$^{2+}$ cations on octahedral sites.

![Figure 5.2: (a) Crystallite size & crystallinity and (b) texture coefficient of magnetic field annealed iron oxide for 120 min.](image)

The crystallite size is extremely sensitive to the concentration of sol as shown in Figure 5.2 (a). The particle growth in a homogenous solution includes three basic steps: 1) nucleation; 2) coalescence of the particles from dissolved species; and 3) growth of particles by the movement of species involving the previously formed bigger particles (Bashir et al. 2014; Riaz and Naseem 2007). In general, sol-gel process is based on polymerization of colloidal particles (Riaz et al. 2011). With increase in concentration (increase in solute/solvent ratio), the number of colloidal particles increases, thus the chances of collision between the particles increase along with increase in electrostatic interactions (Xu et al. 2012). This in turn increases the probability of more and more of the colloidal particles to gather to form larger crystallites. Thus, the crystallite size increases (Riaz et al. 2011). However, in the present condition, more than one phase, i.e., Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ are present in our films. If more than one phase is present in the crystal structure, its properties strongly depend on properties of each phase and also on the way the phase appears in the aggregate (Yanagihara et al. 2013). So, the variation in grain size in our case is strongly affected by the presence of two polymorphs of iron oxide. The important thing to be emphasized here is that all of the films are oriented along (400) plane. However, change of preferred orientation is observed for films with sol concentration of 1.4 mM [Fig. 5.1(c)]. The
preferred orientation changes from (400) to (220) planes and this change of preferred orientation is preserved for 60 and 120 min (MFA). Texture coefficient plotted as a function of sol concentration in Figure 5.2(b) for (400) and (220) planes indicates the crossover of preferred orientation from (400) to (220) as the sol concentration is increased to 1.4 mM.

SEM was used to study the surface morphology of iron oxide structures. Figure 5.3 shows SEM images for the molar concentration in the range of 1.8–0.6 mM. The films deposited with concentration of 1.8 mM [Figure 5.3(a)] show the formation of nanorods with diameter of 70 nm and length 165 nm. Spherical nanoparticles interconnected along with the formation of nanorods are formed with 1.6 mM [Figure 5.3(b)]. Complete transformation from nanorods to nanospheres is observed for sol concentration of 1.4 mM, whereas diameter of the formed nanospheres is 110 nm. With further decrease in molarity to 1.2 mM nanospheres with diameter 200 nm are observed. Nanobrushes with different diameter and length are formed with sol concentration of 1.0, 0.8, and 0.6 mM. It is worth mentioning here that these nanorods and nanobrushes are formed as the result of free growth.
Figure 5.3: SEM images of iron oxide nanostructures deposited with sol concentration. (a) 1.8 mM. (b) 1.6 mM. (c) 1.4 mM. (d) 1.2 mM. (e) 1 mM. (f) 0.8 mM.

Figure 5.4 shows room temperature magnetization curves of iron oxide nanostructures deposited with variation in concentration of the sol. The inset of Figure 5.4 shows magnetization curves for films with a concentration of 1.8 and 1 mM, which show very low saturation magnetization. All the films showed strong ferromagnetic behaviour. However, with increase in sol concentration to 1.4 mM, the ferromagnetic behaviour turns to ferrimagnetic behaviour. This ferrimagnetic behaviour arises due to two reasons. First, there was a change of preferred orientation from (400) to (220) plane as shown in Figure 5.2 (b). Second, there was a transition from mixed magnetite and maghemite to pure magnetite phase [Figure 5.1 (c)] thus leading to pure ferrimagnetic behaviour with high value of saturation magnetization.

Figure 5.4: M–H curves of iron oxide nanostructures.
The saturation magnetization is plotted as a function of sol concentration in Figure 5.5 (a). The value of saturation magnetization is close to that reported for bulk saturation magnetization of Fe$_3$O$_4$ for film deposited using sol concentration of 1.4 mM. However, for rest of the concentration range, the values are less than those of the bulk magnetite.

There can be two reasons for this deviation. First, the presence of secondary phase γ-Fe$_2$O$_3$ lowers the magnetic moment as the reported value of bulk Fe$_3$O$_4$ is 477 emu/cm$^3$ and that of γ-Fe$_2$O$_3$ is 430 emu/cm$^3$ (Hari Babu et al. 2013a). Second, in case of thin films and nanoparticles, the surface to volume ratio increases. The magnetic molecules that are present on the surface are deficient in complete coordination. The spins in turn are disordered at the surface. So, this leads to reduction in saturation magnetization (Schwertmann and Cornell 2008).

The coercivity values of Fe$_3$O$_4$ under 120 min MFA are shown in Figure 5.5(a). Coercivity values, representing the magnetic hardness, depend on both the extrinsic and intrinsic properties of materials (Schwertmann and Cornell 2008). High crystalline anisotropy, an intrinsic property, can be the reason for high coercivity values. Moreover, presence of defects, anti-phase boundaries and dislocations that can hinder the domain wall motion can be a cause of increased coercivity (Celotto et al. 2003). Fe$_3$O$_4$ contains Fe$^{2+}$ and Fe$^{3+}$ cations present on the octahedral and tetrahedral sites. Fe$^{2+}$ and Fe$^{3+}$ cations contain six and five electrons in valence 3d-subshell, respectively.

Figure 5.5: (a) Saturation magnetization & coercivity and (b) μB/f.u. as a function of sol concentration.

According to Hund’s rule, the two electrons are paired and rest of the 4 electrons remain unpaired (Schwertmann and Cornell 2008). So, the contribution of Fe$^{3+}$ cations (5 μB) is greater than that of Fe$^{2+}$ cations (4 μB). Therefore, the total number of Bohr magnetons per formula unit (μB/f.u.) for Fe$_3$O$_4$ should be (4×1) + (5×2) = 14 μB/f.u. But, experimental studies have shown that...
magnetic moment per f.u. for Fe₃O₄ is 4.00 μB/f.u (Schwertmann and Cornell 2008). This is due to the fact that equal numbers of Fe³⁺ cations are arranged in antiparallel fashion on octahedral and tetrahedral sites. So, their magnetic moment cancels out each other and the only contributor to magnetic moment left is Fe²⁺ cations (Schwertmann and Cornell 2008). On the other hand, for γ-Fe₂O₃ the magnetic moment of 2.5 μB/f.u. is due to the vacancies present in cationic sub lattice. For sol concentration of 1.4 mM, the effective Bohr magnetons per formula unit is 3.99 μB/f.u. (Figure 5.5(b)) that is very close to that typical of Fe₃O₄. This strongly indicates the formation of pure magnetite phase. For rest of the concentration range, the values are <4 μB/f.u. but greater than 2.5 μB indicating some contribution from γ-Fe₂O₃ as was also indicated by XRD patterns (Figure 5.1). The Verwey transition in the magnetite thin films with sol concentration of 1.4 mM was found to be around 127 K (Riaz et al. 2013a).

5.5 Summary

Nanocrystalline magnetite nanostructures were prepared using iron (III) chloride by varying sol concentrations. Uniform and homogenous films were achieved on copper substrates using spin coating. XRD measurements showed highly crystalline films with preferred orientation of (400) plane. One exception was the film deposited with sol concentration of 1.4 mM, where the preferred orientation was along (220) plane. It was also seen that this (220) plane played an important role in achieving ferrimagnetic properties. Nanorods and nanobrushes have been reported without the use of any template.
CHAPTER-6
Chapter – 6  Effects of Variation in pH

6.1 Introduction

NPs should be compatible with the living organisms and easily eradicated whereas, biocompatibility of iron oxide has already been proven (Wu et al. 2012a). For biocompatibility, it is very important to avoid their agglomeration by reducing the particle size. Therefore two parameters are of vital importance, the magnetic nanoparticles size and the magnetic interactions among them (Larumbe et al. 2012). By tailoring the size of the magnetite nanoparticles or varying the value of the pH, their magnetic properties can be controlled from superparamagnetic to ferromagnetic (Hashimoto et al. 2012). In the meantime, developments in nanotechnology have enabled the use of a localized and targeted heating source; such heating should cause less damage to the normal cells. The use of ferromagnetic nanoparticles for hyperthermia and thermo-ablation therapy has shown great interest in the field of nanobiotechnology (Kita et al. 2010).

Magnetic properties of NPs differ from those of the bulk materials. Oxide nanocrystallites often have larger coercivities than bulk materials, due to a reinforcement of the surface magnetic anisotropy. A reduction of the saturating magnetization generally occurs in ferromagnetic materials such as α-Fe₂O₃ (hematite) (Brice-Profeta et al. 2005). The size of NPs and their magnetic properties strongly depends upon the synthesis technique.

Different preparation techniques are used in formation of magnetite NPs, including chemical methods (Sol-Gel, Co-Precipitation, and Hydrothermal) or Physical methods (laser ablation, mechanical ball milling, sputtering) (Larumbe et al. 2012; Lévy et al. 2008). In this research work, we have synthesized nanoparticles of iron oxide by sol-gel at different pH values. The variation in magnetic and structural behavior is correlated with pH.

6.2 Experimental Details

6.2.1 Materials

Iron (III) nitrate (Sigma-Aldrich, 99.99% pure) and ethylene glycol (Sigma-Aldrich, 99.99% pure) were used without purification. Water was deionized prior to use.
6.2.2 Magnetic Nanoparticle Synthesis

Different solutions were prepared by varying the amount of NaOH to control pH while the amount of iron (III) nitrate was constant in all solutions. Iron (III) nitrate was added into ethylene glycol and was subjected to vigorous stirring at 40°C for sol formation. 2M NaOH was added dropwise to vary pH from 1 to 9. These sols were heated at 80°C under constant stirring until gels were obtained. The resultant gels were aged for 2 h and then dried at 120 °C for 4 h. Obtained powders were washed several times with deionized water until negative chlorine test appeared. Schematic approach for preparation of iron oxide nanoparticles is illustrated in Figure 6.1.

After the formation of iron oxide nanoparticles with pH variation, 9 pellets were formed by applying half-ton force. These nanoparticles were then calcined at 200 °C and 300 °C both in the absence and presence of magnetic field of 500Oe, respectively.

![Schematic Approach for Preparation of Iron Oxide Nanoparticles](image)

**Figure 6.1: Schematic Approach for Iron Oxide nanoparticles.**

6.2.3 Characterization

A wide-angle X-ray diffractometer (Bruker D8 da vinci) was used to study the crystalline structure of the NPs. The Cu K-alpha radiation source was used. K-beta filter was used to eliminate interference peak. Scanning electron microscope (Hitachi, S3400N) was used to investigate the morphological structure and to measure the particle size of the iron oxide NPs. Vibrating sample magnetometer (LakeShore, Series 7400 model 7407) was used to study the magnetic properties of the magnetite nanoparticles. The hysteresis loops were measured under a magnetic field strength of 1T at room temperature.
6.3 Results and Discussion

6.3.1 Structural Properties

Structure, phase, crystallite size and crystallinity of the synthesized nanoparticles were investigated by XRD. Figures 6.2 & 6.3 show the XRD patterns of the as-synthesized and annealed samples at pH 1 & pH 2 in the absence and presence of magnetic field. Presence of peaks at angles (2θ) of 30.0°, 35.4°, 43.0°, 57.0°, and 63.0°, corresponding to (220), (311), (400), (511) and (440), planes show the formation of Fe$_3$O$_4$ phase at pH 1 (JCPDS card No. 85-1436). Whereas, appearance of (222), (422), (440) and (620) planes confirm the presence of Fe$_3$O$_4$ phase at pH 2. Fe$_3$O$_4$ phase appeared under as-synthesized condition persisted after annealing at 200 and 300 °C. However, strengthening of Fe$_3$O$_4$ phase was observed after annealing the samples at these temperatures in the presence of magnetic field.

Figure 6.2: XRD patterns for iron oxide nanoparticles synthesized at pH 1.

Figure 6.3: XRD patterns for iron oxide nanoparticles synthesized at pH 2.
Increase in pH of iron oxide sol to 3-5 resulted in the formation of α-Fe₂O₃ as shown in Figures 6.4-6.6 (a and b). α-Fe₂O₃ (hematite) phase might have appeared because of the change in Fe²⁺ and Fe³⁺ ratios due to the increased pH value.

Figure 6.4: XRD patterns for iron oxide nanoparticles synthesized at pH 3.

Figure 6.5: XRD patterns for iron oxide nanoparticles synthesized at pH 4.

Figure 6.6: XRD patterns for iron oxide nanoparticles synthesized at pH 5.
Further increase in pH up to 6 led to the re-appearance of magnetite phase with (220), (400), (422), (440) and (533) planes as shown in Figure 6.7 (a) and (b). Strengthening of magnetite phase (Fe$_3$O$_4$) was observed after annealing the samples in the presence of magnetic field.

Figure 6.7: XRD patterns for iron oxide nanoparticles synthesized at pH 6.

The broad peaks in XRD patterns of samples synthesized with pH 7 and pH 8 suggest the nanocrystalline nature of maghemite nanoparticles as shown in Figure 6.8 and Figure 6.9. For samples with pH 7 and pH 8, obtained peaks (210), (221), (310), (222), (320) and (400) correspond to the inverse cubic spinel structure of maghemite (JCPDS Card No. 39-1346).

Figure 6.8: XRD patterns for iron oxide nanoparticles synthesized at pH 7.
Mixed behavior i.e. presence of hematite and maghemite in samples with pH 9 was obtained as given in Figure 6.10. In as-synthesized conditions maghemite was obtained while with increase in calcination temperature (absence of magnetic field) maghemite transformed into hematite. Shift in the characteristic peak (221) in as-synthesized and calcined at 200 °C samples confirms this transformation with presence of characteristic peak (104) for hematite in case of calcination at 300 °C in the presence and absence of magnetic field.

Lattice parameters and unit cell volume for magnetite and maghemite with cubic spinel structure was calculated by Equations 6.1 and 6.2, respectively (Culity and Stock 1978).
\[
\frac{1}{d^2} = \frac{k^2 + k^2 + l^2}{a^2} \quad (6.1)
\]
\[
v = a^3 \quad (6.2)
\]

Where hkl are the miller indices, d is the inter-planer spacing and v is the unit cell volume of cubic crystal with a as lattice parameter.

Lattice parameters and unit cell volume for hematite, with hexagonal corundum like crystal structure were calculated by Equations 6.3 and 6.4, respectively.

\[
\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + k^2 + hl) + \frac{\lambda^2 l^2}{4c^2} \quad (6.3)
\]

\[
v = 0.866a^2c \quad (6.4)
\]

The calculated values, using above relations are tabulated in Tables 6.1 (a-d).

Table 6.1a. Lattice parameters of iron oxide nanoparticles synthesized at different pH (1-4)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>pH 1</th>
<th>pH 2</th>
<th>pH 3</th>
<th>pH 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>a(Å)</td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td>As-syn</td>
<td>8.363</td>
<td>8.369</td>
<td>5.0451</td>
<td>13.795</td>
</tr>
<tr>
<td>300ºC</td>
<td>8.3745</td>
<td>8.375</td>
<td>5.098</td>
<td>13.8102</td>
</tr>
<tr>
<td>200ºC MF</td>
<td>8.365</td>
<td>8.374</td>
<td>5.087</td>
<td>13.8135</td>
</tr>
<tr>
<td>300ºC MF</td>
<td>8.374</td>
<td>8.379</td>
<td>5.1035</td>
<td>13.8235</td>
</tr>
</tbody>
</table>
Table 6.1b. Lattice parameters of iron oxide nanoparticles synthesized at different pH (5-9)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>c(Å)</td>
<td>a(Å)</td>
<td>a(Å)</td>
<td>a(Å)</td>
<td>a(Å)</td>
</tr>
<tr>
<td>As-syn</td>
<td>5.10632</td>
<td>13.9145</td>
<td>8.375</td>
<td>8.359</td>
<td>8.3813</td>
</tr>
<tr>
<td>200°C</td>
<td>5.1148</td>
<td>13.9205</td>
<td>8.379</td>
<td>8.361</td>
<td>8.3914</td>
</tr>
<tr>
<td>300°C</td>
<td>5.1298</td>
<td>13.9507</td>
<td>8.3805</td>
<td>8.3624</td>
<td>8.3999</td>
</tr>
<tr>
<td>200°C MF</td>
<td>5.1354</td>
<td>13.9287</td>
<td>8.3765</td>
<td>8.3698</td>
<td>8.3824</td>
</tr>
</tbody>
</table>

Table 6.1c. Unit cell Volume of iron oxide nanoparticles synthesized at different pH (1-4)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>pH 1</th>
<th>pH 2</th>
<th>pH 3</th>
<th>pH 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit cell volume (Å³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-syn</td>
<td>584.9063</td>
<td>586.1661</td>
<td>304.0739</td>
<td>309.7283</td>
</tr>
<tr>
<td>200°C</td>
<td>585.2211</td>
<td>586.5864</td>
<td>306.2143</td>
<td>311.606</td>
</tr>
<tr>
<td>300°C</td>
<td>587.3225</td>
<td>587.4277</td>
<td>310.8261</td>
<td>312.1499</td>
</tr>
<tr>
<td>200°C MF</td>
<td>585.326</td>
<td>587.2173</td>
<td>309.5602</td>
<td>312.2</td>
</tr>
<tr>
<td>300°C MF</td>
<td>587.2173</td>
<td>588.2698</td>
<td>311.7972</td>
<td>314.3292</td>
</tr>
</tbody>
</table>
The peak broadening of XRD reflection can be used to estimate the crystallite size on the basis of Scherrer’s equation as given in Equation (6.5):

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(6.5)

Where \( k \) is a grain shape dependent constant (here assumed to be 0.89 for spherical particles), \( D \) is the crystallite size (nm), \( \lambda \) is the wavelength of X-ray beam, \( \beta \) is the full width at half maximum for the diffraction peak under consideration (in radians), and \( \theta \) is the diffraction angle.

The variation of crystallite size for iron oxide nanoparticles prepared under as-synthesized and calcination conditions (200°C, 300°C, 200°C MF and 300°C MF) with variation in pH is given as in Figure 6.11 to Figure 6.19.

Relatively larger increase in crystallite size after magnetic field annealing is the evidence of strengthening of iron oxide phase appearing under as-synthesized condition at pH 1-8. However, at pH9 restructuring of phases appeared resulting in decrease of crystallite size. This restructuring resulted in the transformation of \( \gamma \)-Fe\(_2\)O\(_3\) phase to \( \alpha \)-Fe\(_2\)O\(_3\) phase.

Same trend for all the samples was observed except for sample synthesized with pH 9 in which both hematite and maghemite phases were present. The presence of these two phases results in the reduction of crystallite size in both cases of calcination i.e. with and without the presence of magnetic field.
Figure 6.11: Crystallite size for iron oxide nanoparticles synthesized at pH 1.

Figure 6.12: Crystallite size for iron oxide nanoparticles synthesized at pH 2.

Figure 6.13: Crystallite size for iron oxide nanoparticles synthesized at pH 3.
Figure 6.14: Crystallite size for iron oxide nanoparticles synthesized at pH 4.

Figure 6.15: Crystallite size for iron oxide nanoparticles synthesized at pH 5.

Figure 6.16: Crystallite size for iron oxide nanoparticles synthesized at pH 6.
Figure 6.17: Crystallite size for iron oxide nanoparticles synthesized at pH 7.

Figure 6.18: Crystallite size for iron oxide nanoparticles synthesized at pH 8.

Figure 6.19: Crystallite size for iron oxide nanoparticles synthesized at pH 9.
6.3.2 Morphological Properties

The sol-gel technique offers many opportunities for controlling particle size and morphology by keeping residence times low and mixing processes efficient. It appears that increasing the pH favors the formation of spherically shaped particles as shown in Figure 6.20 (a-e).

![Figure 6.20: SEM micrographs of iron oxide nanoparticles with variation in pH 1, 3, 6, 7 & 9 in a – e respectively.](image)

At pH 1 and pH 2, size of magnetite nanoparticle is 50 nm (Figure 6.20a) but for the hematite nanoparticles at pH 3 are less than 10nm in size as shown in Figure 6.20b. However, SEM results show the formation of comparatively larger size for magnetite nanoparticles at pH 6. Figure 6.20d shows maghemite nanoparticles of diameter 100 nm synthesized at pH 7. At higher pH 9, aggregation occurs resulting in clusters due to hydrophobic nature of particles (Figure 6.20e); this correlates well with the XRD results where presence of multiple phases was shown.

The variation in grain size by change in pH of the sol arises from the fact that articles with small sizes are favored due to greater surface energy in reaction dynamics, while those particles that are with larger sizes are thermodynamically favored due to larger volume energy. Larger nanoparticles are formed in the synthesis process because the smaller nuclei dissolve to attain critical nuclear size. Hence, critical size increases with increased pH of the reaction. As with the
increase in pH oxidation ratio decreases due to increase in concentration of Fe\(^{2+}\) ions as shown in the XRD data. Hence by controlling pH particle size can be controlled for different phases.

### 6.3.3 Raman Analysis

In order to confirm the formation of magnetite, maghemite and hematite at different pH values Raman analysis was carried out as shown in Figure 6.21 (a-i). Raman analysis also confirms the formation of magnetite phase at pH 1, 2 and 6, which is in accordance to the XRD results.

Equation (6.6) shows the active vibrational Raman modes for magnetite in the first Brillouin zone (Rana and Johri 2014).

\[
\Gamma_{\text{vib}} = A_{1g} + 3T_{2g} + E_{1g}
\]

(6.6)

Where, \(A_{1g}\) defines the presence of symmetric stretching of oxygen atoms in iron-oxygen bond. \(3T_{2g}\) and \(E_{1g}\) indicate presence of asymmetric and symmetric oxygen bonds relative to those of iron (Shebanova and Lazor 2003).
Figure 6.21: Raman analysis of iron oxide nanoparticles with pH Variation.
Whereas T_{1g}, E_{u}, T_{2u} and A_{2u} are known as the optically silent modes of magnetite and this detail of vibrational modes also involves one infrared active mode of magnetite i.e. 4T_{1u} (Rana and Johri 2014). Presence of Raman mode at 552, 667 and 668 cm\(^{-1}\) in samples with pH 1, 2 and 6 respectively confirms magnetite formation (Figure 6.24 a and b) (Shebanova and Lazor 2003). In case of magnetite Raman peaks in the range of 460-660 cm\(^{-1}\) are due to octahedral group i.e. O-site is active in this case, while in case of active tetrahedral site Raman peaks for magnetite will be in the range of 660-720 cm\(^{-1}\) (Rana and Johri 2014).

At pH 3, 4 and 5 hematite phase was confirmed by the presence of Raman bands at 293, 293 and 291 cm\(^{-1}\). At high pH, transformation to magnetite was also confirmed from the band present at 668 cm\(^{-1}\). At pH 7 and 8 maghemite phase with Raman modes at 350, 700 and 707 cm\(^{-1}\) were obtained while in case of pH 9 presence of characteristic band of hematite at 293 cm\(^{-1}\) and at 351 cm\(^{-1}\) for maghemite confirms the presence of mixed phases, which is also confirmed from XRD data.

### 6.3.4 Optical Band Gap

Figure 6.22 gives the band gap variation with pH.

![Figure 6.22: Variation of band gap for pH 1-9.](image)

### 6.3.5 Magnetic Properties

Magnetic properties measured at room temperature for nanoparticles synthesized at pH 1-9 are shown in Figure 6.23-6.31 (a) and (b), respectively. The M-H curves for pH 1 and 2 exhibit the superparamagnetic nature as shown in Figure 6.23-6.24 (a) and (b). In our case calcination only
strengthen the already synthesized phases except for the case of pH 9 in which calcination results in phase transformation from hematite to maghemite.

Figure 6.23: M-H curves for iron oxide nanoparticles synthesized with pH 1 and (a) annealed at 200˚C and 300˚C; (b) MF annealed at 200˚C and 300˚C.

Figure 6.24: M-H curves for iron oxide nanoparticles synthesized with pH 2 and (a) annealed at 200˚C and 300˚C; (b) MF annealed at 200˚C and 300˚C.

Superparamagnetic behavior is attributed to the smaller particle size of magnetite nanoparticles i.e. with high value of saturation magnetization of 96 emu/g, which is larger value of saturation magnetization reported in literature i.e. 75.3 emu/g.
Figure 6.25: M-H curves for iron oxide nanoparticles synthesized with pH 3 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.

Figure 6.26: M-H curves for iron oxide nanoparticles synthesized with pH 4 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.

Figure 6.27: M-H curves for iron oxide nanoparticles synthesized with pH 5 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.
Figure 6.28: M-H curves for iron oxide nanoparticles synthesized with pH 5 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.

Figure 6.29: M-H curves for iron oxide nanoparticles synthesized with pH 7 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.

Figure 6.30: M-H curves for iron oxide nanoparticles synthesized with pH 8 and (a) annealed at 200°C and 300°C; (b) MF annealed at 200°C and 300°C.
Saturation magnetization values (Ms) of iron oxide nanoparticles obtained at pH values 1-9 are depicted in Figures 6.32-6.40, respectively.

**Fig. 6.32:** Saturation magnetization for iron oxide nanoparticles synthesized with pH 1.
Figure 6.33: Saturation magnetization for iron oxide nanoparticles synthesized with pH 2.

Figure 6.34: Saturation magnetization for iron oxide nanoparticles synthesized with pH 3.

Figure 6.35: Saturation magnetization for iron oxide nanoparticles synthesized with pH 4.
Figure 6.36: Saturation magnetization for iron oxide nanoparticles synthesized with pH 5.

Figure 6.37: Saturation magnetization for iron oxide nanoparticles synthesized with pH 6.

Figure 6.38: Saturation magnetization for iron oxide nanoparticles synthesized with pH 7.
Remarkable increase in saturation magnetization was observed at pH 1-8 after annealing the samples in the presence of magnetic field. These magnetization results are in agreement with the structural behavior of iron oxide nanoparticles observed in Figures 6.2-6.10. Magnetic field helped in aligning the domains already present in the material thus resulting in larger values of Ms as compared to the samples annealed in the absence of magnetic field. However, decrease in Ms with increase of pH to 9 is indicative of the transition of pre-existed iron oxide phase. This result is in close agreement with XRD results of Figure 6.10 showing transformation of $\gamma$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$ phase after annealing at 300 °C.

With regard to use of ferromagnetic NPs as heat generation materials, the hysteretic behavior plays particularly important role. While dealing with iron oxide nanoparticles without surface
coating, the surface of these nanoparticles behaves like hydrophobic. As a result of hydrophobic interactions among these nanoparticles with large surface area, agglomeration occurred. At the end of this process nanoparticles with larger size were obtained with ferromagnetic behavior due to strong magnetic dipole–dipole attractions (Riaz et al. 2014e).

6.4 Summary

In this section, iron oxide nanoparticles have been reported to be synthesized by varying the pH from 1 to 9. Fe₃O₄ phase was observed at pH 1, 2 & 6 under all the annealing conditions. α-Fe₂O₃ phase was observed at pH 3-5. Whereas, increase in pH of 7-8 led to the formation of Y-Fe₂O₃ phase before and after annealing. Moreover, pH 9 led to transformation of Y-Fe₂O₃ phase to α-Fe₂O₃ phase after annealing at 300 °C. Magnetic properties were strongly influenced by pH. Superparamagntic behavior to ferromagnetic nature has been observed due to reduction of Fe³⁺ ions and vacancies at sublattices. SEM showed the formation of nanoparticles non-interacting in case of pH 1 (superparamagnetic) and interacting (ferromagnetic) or diffused at higher pH values. However, 50 nm of particles size along with spherical shape was observed, preferable for biomedical applications.
CHAPTER-7
Chapter – 7 Effects of Variation of Surfactant

7.1 Introduction

Iron oxide nanoparticles have their applications in magnetic recording media as well as in biomedical and biological areas (Akbar et al. 2014a; Andersson et al. 2015; Babay et al. 2015; Riaz et al. 2014b). However, the limitation for their use in above applications is the controlled growth of these nanoparticles with precise morphology (Jiang et al. 2014; Riaz et al. 2014a; Riaz et al. 2014d; Soares et al. 2014). Among various materials of interest, magnetite nanoparticles are most widely studied and used due to their superparamagnetic properties at room temperature with high saturation magnetization, their non-toxic nature and high biocompatibility (Riaz et al. 2014a; Riaz et al. 2014d). Magnetite has found its biomedical applications in MRI contrast agent, targeted drug delivery, hyperthermia, cancer therapy etc. (Lukashova et al. 2014; Riaz et al. 2014a; Riaz et al. 2014d; Soares et al. 2014). For these applications magnetite nanoparticles with less than 128nm size is required as below this size magnetite nanoparticles shows superparamagnetic behavior with single domain. Nanoparticles above this critical size will only react with cell and will be unable to cross the vessels. (Petcharoen and Sirivat 2012; Riaz et al. 2014a; Riaz et al. 2014d).

Agglomeration of magnetite nanoparticles also causes the reduction of their use in various biomedical applications. Anisotropic dipolar interaction is the main cause of this agglomeration (Lu et al. 2002; Riaz et al. 2014a). Hence, to avoid this agglomeration surfactants are required (Lu et al. 2002).

We here report synthesis of pure magnetite nanoparticles for their application in biomedical field. Sol-gel method was used for synthesis, and effect of surfactant and calcination temperature was observed.

7.2 Materials and Methods

Magnetite nanoparticles were synthesized by making two solutions as described in Chapter 5, section 5.2. For solution 1, FeCl₃.6H₂O, (99.9% pure) was dissolved in deionized water. Solution 1 was finally achieved by dissolving it further in 99.98% pure n-Hexane. While for the synthesis of solution 2, NaOH was mixed in ethanol. After the mixing of these two solutions magnetic stirring at 50°C was done to remove the two distinguishable layers (formed after mixing solution 1 and solution 2) and obtain sol with single layer.
In order to obtain magnetite in the superparamagnetic form, it was decided to change the surfactant. PVA, triton X-100 and oleic acid were used to optimize the conditions under which a particular surfactant can help achieve the goal. Results (discussed below) confirmed that oleic acid was the best surfactant for these nanostructures, and hence the details are given for only oleic acid.

The sols were then aged and after aging iron oxide sols were obtained by the addition of different volumes of oleic acid at 55°C. Equation (7.1) gives the detailed steps involved in the formation of magnetite.

\[
\begin{align*}
FeCl_3 + 3H^+OH & \rightarrow Fe(OH)_3 + 3HCl \\
Fe^{3+} + e^- & \rightarrow Fe^{2+} \\
Fe^{2+} + OH & \rightarrow Fe(OH)_2 \\
3Fe(OH)_2 + \frac{1}{2}O_2 & \rightarrow Fe(OH)_3 + 2FeOOH + H_2O \\
Fe(OH)_2 + 2FeOOH & \rightarrow Fe_3O_4 + 2H_2O
\end{align*}
\]

Reduction of Fe\(^{3+}\) ions into Fe\(^{2+}\) ions is the main cause of formation of Fe(OH)_2 which results in the formation of FeOOH after partial oxidation. This results in the production of magnetite. In this reaction in order to speed up the reaction and for the compensation of strong base, NaOH and n-hexane were used, respectively.

Selection of appropriate surfactant is enormously essential in the synthesis of iron oxide sol with maximum stability. Primarily surfactants are added in the monomer solution due to their ability of making intermediate complexes, which results in the delay of nucleation. Furthermore, they can form a protecting monolayer. Based on these facts choice of surfactant requires mainly as it does not resist the process of nucleation also it must prevent the formation of aggregation of nanoparticles. Oleic acid (with formula \(CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H\)) results in pure magnetite by working as surfactant. The presence of double bond at position 9 and position 10, as shown in Figure 7.1, is responsible for stability of magnetite nanoparticles. (Lu et al. 2007; Zhang et al. 2006).

Sol was then further processed to obtain gel. The gel was then calcined at 300°C to 900°C with 200°C increase in temperature for 60mins to obtain iron oxide nanoparticles. Along with variation in calcination temperature amount of oleic acid was also varied during sol synthesis.
As a result of variation in (5, 10 and 15) volume % of oleic acid, three sols were synthesized. Sol A for 5% oleic acid, Sol B with 10% and Sol C with 15% oleic acid.

### 7.3 Results and Discussion

Figure 7.2 (c) shows magnetization curve for Sol-C. Superparamagnetic behavior for Sol-C confirms the full development of magnetic domains in Sol C. This is also indicated by negligible value of remanace and coercivity of the same sol. Hence nanoparticles synthesized by using this sol can be used in those biomedical applications for which superparamagnetic nature of synthesized magnetite nanoparticles is a critical requirement. While diamagnetic, paramagnetic or mixed behavior, as shown in Figure 7.2, is observed in case of rest of the Sol-s. It should be mentioned here that Sols D – G were prepared using poly vinyl alcohol (PVA) and triton X-100 as surfactants; Figure 7.2 (e&g) are for the aged sols. It becomes evident from the magnetic properties of the sols prepared with various surfactants that the sol prepared with oleic acid were to be used for synthesis of nanostructures for biomedical applications.
Figure 7.2: Magnetic hysteresis curves for iron oxide sols obtained at room temperature a) Sol A, b) Sol B, c) Sol C, d) Sol D, e) Sol E, f) Sol F and g) Sol G.
Figures 7.3 & 7.4 show XRD patterns of iron oxide nanostructures prepared by the above-mentioned procedures using PVA and triton X-100 as surfactant. It can be seen from these figures that the final product is either amorphous or is composed of mixed phases of iron oxide.

Figure 7.3: XRD patterns of iron oxide nanoparticles synthesized by Sol E with PVA as surfactant.

Figure 7.4: XRD patterns of iron oxide nanoparticles synthesized by Sol-G with triton X-100 as surfactant.

Figure 7.5(a) and (b) shows XRD patterns of iron oxide nanoparticles synthesized from Sol B and Sol C, respectively. These are results obtained at calcination temperature of 300°C-900°C (with increase of 200°C). Mixed phases (with dominant Fe₃O₄ and γ-Fe₂O₃ inverse spinel structure and minor contribution of α-Fe₂O₃) are obtained for the nanoparticles synthesized by Sol B. However, increased calcination temperature results in decreased contribution of α-Fe₂O₃.
This decrease of $\alpha$-$\text{Fe}_2\text{O}_3$ is also confirmed by decrease in the peak intensities with increase in calcination temperature. Presence of $\alpha$-$\text{Fe}_2\text{O}_3$ at higher temperatures in Figure 7.5 (a) shows that calcination is not responsible for complete elimination of this phase. Also, formation of $\alpha$-$\text{Fe}_2\text{O}_3$ is not due to calcination temperature.

Presence of (220), (311) and (222) planes confirms the formation of single-phase magnetite even at 300°C (JCPDS Card No. 72-2303). Further increase in calcination to 900°C does not show any peak corresponding to hematite and/or maghemite in case of Figure 7.5(b). Increased peak intensities indicate the increased crystallinity of magnetite nanoparticles with increased calcination temperature from 300°C to 500°C, while decrease in peak intensities is obtained when calcination temperature was further increased. In addition, absence of new diffraction peaks at lower 20° values i.e. < 30° (Figure 7.5(b)), eliminates the possibility of magnetite to maghemite conversion.

![XRD patterns of a) iron oxide nanoparticles synthesized by Sol B, b) iron oxide nanoparticles synthesized by Sol-C.](image1)

Lattice parameters calculated using XRD are plotted as a function of calcination temperature in Figure 7.6(a) and are found to be 8.38Å with no significant change in lattice constants with calcination temperature. The low lattice constants values and consequently the low unit cell volume (Figure 7.6(b)) of nanoparticles prepared using Sol B is due to the presence of mixed phases as can be seen in Figure 7.5(a).
Figure 7.6: (a) Lattice constants; b) Unit cell volume of iron oxide nanoparticles calculated with increasing calcination temperature.

Evaluation of XRD patterns (Figure 7.5 (a-b)) of iron oxide nanoparticles synthesized by Sol B and Sol C indicates that single pure phase of magnetite with improved crystallinity can be achieved with increased oleic acid concentration. Stability of the synthesized magnetite phase is owing to the addition of precise amount of oleic acid, which results in the formation of the protective coating around the synthesized magnetite nanoparticles. Surface oxidation and surface anisotropy of the nanoparticles as well as particle interaction is also reduced by this protective coating.

Variation in crystallite size with increase in calcination temperature for nanoparticles with Sol B and Sol C is given in Figure 7.7 (a). Crystallite size is calculated by XRD graphs. Figure 7.7 (b) shows that specific area for both types of nanoparticles is also calculated by XRD and is plotted against increase in calcination temperature. Low crystallinity of magnetite nanoparticles at 500°C is obtained. Similar trend for both crystallite size and specific surface area is obtained for both
types of nanoparticles i.e. prepared with Sol B and Sol C. Further increase in crystallite site above 500 °C is due to grain growth which is because of Ostwald ripening mechanism.

Figure 7.7: (a) Variation in crystallite size with calcination temperature (b) Variation in specific Surface Area with calcination temperature.

Surface morphology of nanoparticles synthesized with three different sols was studied by SEM. Sample synthesized by Sol A (after calcination at 500°C) confirms the formation of mix shaped nano-spheres having diameter greater or equal to 250nm. The random size distribution and variation in size, as shown in Figure 7.8, are due to presence of mixed phases in Sol A. With further increase in concentration of oleic acid to 10% these mixed and random shaped nanoparticles converted to spherical shaped nanoparticles with definite sizes after calcination at different temperatures. Figure 7.9 (a-c) shows SEM micrographs of nanoparticles synthesized from Sol B calcined at 300°C, 500°C and 700°C, respectively.

Figure 7.8: SEM image of iron oxide nanoparticles prepared with sol A.
Spherical nanoparticles with 80 nm and 180nm diameter are obtained when calcination at 300°C was carried out. Furthermore these nanoparticles were consists of mixture of two types on the basis of shell formation i.e. nanoparticles with shell were obtained with diameter of 180nm while nanoparticles without shell were obtained with diameter of 80nm. The morphology of the nanoparticles remained same with increase in calcination temperature but decreased particles size i.e. 50-120nm was obtained as compared to 80-180nm. Nanoparticles with 50-180nm diameter were observed without shell spherical morphology for the case of further increase in calcination to 700°C (Figure 7.9 (c)).

For the nanoparticles synthesized with 15% increased volume concentration of oleic acid, size and morphology of the synthesized nanoparticles were changed. Spherical to cubic morphology was obtained as shown in Figure 7.10 (a). This change in shape might be because of the formation of single-phase magnetite. When these nanoparticles were calcined at 500°C, reduction in size to 18 nm was obtained while further increase in calcination temperature resulted in
increased size with preserved morphology. Reduction in particle size (less than 50nm) leads to superparamagnetic behavior of magnetite, which results in their use in biomedical applications.

Figure 7.10: SEM images of iron oxide nanoparticles synthesized using Sol C at calcination temperature of (a) 300˚C (b) 500˚C (c) 700˚C and (d) 900˚C.

M-H curve of nanoparticles prepared form Sol A and calcined at 300˚C shows para-ferromagnetic mixed behavior as can be seen in Figure 7.11(a). This mixed behavior was due to dia-ferromagnetic nature of sol itself (Figure 7.2) that resulted in the presence of mixed phases. Mixed behavior of nanoparticles shows that the magnetic domains are not fully developed and the exchange field between the multiple grains is not sufficient enough to produce saturation in the sample. However at 500˚C and 700˚C pure ferromagnetic behavior was observed. When the nanoparticles were calcined at 900˚C again a mixed behavior was observed indicating that the grains were disordered to such an extent that they hardly prove their existence in magnetism.

With increase in oleic acid content in Sol-B, nanoparticles calcined at 300˚C showed weak ferromagnetic behavior (Figure 7.11 (b)). This behavior improved a lot as compared to the mixed behavior observed for nanoparticles prepared from Sol-A and calcination at 300˚C (Figure
This better behavior is due to para-ferroamgentic nature of Sol-B as compared to diaferromagnetic nature of Sol-A (Figure 7.2). This mixed behavior can be because of the presence of mixed phases of iron oxide as seen in Figure 7.3(a). At 500°C pure ferromagnetic behavior was observed that is indicative of large particle size as was observed in the SEM images of Figure 7.9. Higher value of saturation magnetization was obtained as compared to that obtained from Sol A after calcination at 500°C. Calcination at 500°C results in best ferromagnetic properties while reduction in saturation magnetization is obtained with calcination at 700°C. Mixed behavior of shape and size (Figure 7.9) along with decrease in crystallinity (Figure 7.5) of these nanoparticles at 700°C results in decrease of saturation magnetization. Mixed magnetic behavior of nanoparticles calcined at 900°C results due to distortion in morphologies obtained at 500°C and 700°C. Magnetic properties of these nanoparticles, synthesized with variation in volume concentration of oleic acid, are strongly correlated with their structural and morphological properties obtained by XRD and SEM. Weak magnetic properties at calcination of 900°C might be due to random distribution of different nanoparticles as shown from SEM images.

Best magnetic properties of magnetite NPs were observed in case of Sol-C. The improved magnetic properties observed in case of Sol-C are due to superparamagnetic nature of sol (Figure 7.2) that leads to nanoparticles of uniform size and shape thus leading to better magnetic properties as compared to Sol-A and Sol-B. Even at 300°C the NPs show pure ferromagnetic behavior demonstrating single-phase magnetite. Increasing the calcination temperature to 500°C superparamagnetic behavior was attained. This superparamagnetic behavior and increase of saturation magnetization is indicative of strengthening of magnetite phase as was observed in Figure 7.5 (b).

Further increasing the calcination temperature reduces saturation magnetization but the particles still show ferromagnetic behavior due to increase in particle size and decrease in crystallinity as the peak intensities decrease in XRD (Figure 7.5). Ferromagnetic behavior even at 900°C is due to the fact that magnetic domains were already present within the sol and the resulting exchange interactions are strong enough to produce saturation.

Saturation magnetization $M_s$ is plotted as a function of calcination temperature, in Figure 7.12, for the nanoparticles prepared using Sol-A, Sol-B and Sol-C. It can be seen in Figure 7.12 that oleic acid content has a strong impact on saturation magnetization of nanoparticles.
High oleic acid in sol results in formation of protective layer around iron oxide nanoparticles thus preventing oxidation of iron oxide nanoparticles. This resulted in high saturation magnetization of nanoparticles prepared with sol-C as compared to that prepared using sol-A and B.

Figure 7.12: Comparison of Saturation Magnetization of nanoparticles prepared using Sol-A, Sol-B and Sol-C.
Comparison of structural and magnetic properties of iron oxide nanoparticles prepared from three different sols with variation in content of oleic acid from 5% to 15% by volume is listed in Table 7.1. It can be seen that development of magnetic domains within the sol itself strongly affects the structural as well as magnetic properties of sol. With increase in concentration of oleic acid the nanoparticles showed a transition from mixed iron oxide phases to pure highly crystalline magnetite phase. This indicates that controlled addition of oleic acid prevents oxidation of nanoparticles thus stabilizing the magnetite phase. Moreover, it not only reduces the particle size from 200nm to 18nm but also has a tremendous effect on shape of nanoparticles. These changes in phase stability, crystallinity, shape and size altogether affect the magnetic properties and help in obtaining superparamagnetic behavior that is an essential requirement for NPs to be used for biomedical applications.

**TABLE 7.1: Comparison of structural and magnetic properties of iron oxide NPs**

<table>
<thead>
<tr>
<th>Sol used</th>
<th>Calcination Temperature (°C)</th>
<th>Shape of nanoparticles</th>
<th>Size (nm)</th>
<th>$M_s$ (emu)</th>
<th>$H_c$ (Gauss)</th>
<th>Magnetic Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>Random distribution</td>
<td></td>
<td>--</td>
<td>--</td>
<td>Par- ferromagnetic</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>0.0012</td>
<td>400</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td></td>
<td>0.00025</td>
<td>200</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td>--</td>
<td>--</td>
<td></td>
<td>Par- ferromagnetic</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>Spherical with and without shell</td>
<td>180, 80</td>
<td>0.018</td>
<td>263</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>0.025</td>
<td>344</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>700</td>
<td>Random Distribution</td>
<td></td>
<td></td>
<td>--</td>
<td></td>
<td>Par- ferromagnetic</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td>--</td>
<td></td>
<td>Par- ferromagnetic</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>Cubic</td>
<td>$\geq 100$</td>
<td>0.02</td>
<td>360</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>18</td>
<td>0.06</td>
<td>8</td>
<td></td>
<td>Superparamagnetic</td>
</tr>
<tr>
<td>700</td>
<td>$\geq 250$</td>
<td></td>
<td>0.038</td>
<td>294</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>900</td>
<td>Random Distribution</td>
<td></td>
<td>0.03</td>
<td>350</td>
<td></td>
<td>Ferromagnetic</td>
</tr>
</tbody>
</table>

Dielectric constant $\varepsilon$ and tangent loss ($\tan\delta$) for iron oxide nanoparticles were calculated using Equations (7.2) and (7.3) (Barsoukov and Macdonald 2005).

$$\varepsilon = \frac{Cd}{\varepsilon_o A}$$  \hspace{1cm} (7.2)

$$\tan\delta = \frac{1}{2\pi\varepsilon\varepsilon_o\rho}$$  \hspace{1cm} (7.3)
Where, $C$ represents capacitance of nanoparticles under parallel plate configuration, $d$ and $A$ represent thickness and area of specimen, $f$ is the externally applied frequency and $\varepsilon_0$ represents permittivity of free space. Dielectric constant and tangent loss are plotted as a function of $\log f$ in Figures 7.13-7.15. Decrease in dielectric constant (Figure 7.13(a), 7.14(a), 7.15(a)) and tangent loss (Figure 7.13(b), 7.14(b), 7.15(b)) is rapid at low frequencies and becomes slow in high frequency region and then becomes constant. When the frequency of externally applied electric field is less than the jumping frequency of electrons between Fe$^{3+}$ and Fe$^{2+}$ cations on the octahedral sites the electrons are able to follow the alterations in the applied field. This results in high polarization and hence high dielectric constant at low frequencies. This jumping of electrons on octahedral sites also results in high-energy losses and hence high tangent loss at low frequencies.

![Figure 7.13: (a) Dielectric constant (b) Tangent loss for iron oxide nanoparticles synthesized using Sol-A.](image1)

![Figure 7.14: (a) Dielectric constant (b) Tangent loss for iron oxide nanoparticles synthesized using Sol-B.](image2)
When frequency of externally applied electric field becomes higher than the jumping frequency of electrons the electrons do not get the opportunity to jump from Fe$^{3+}$ cations to Fe$^{2+}$ cations before field reversal takes place. This results in decrease of both dielectric constant and tangent loss at high frequencies (Barsoukov and Macdonald 2005; El Hiti 1999; Majid et al. 2015; Riaz et al. 2015).

Dielectric constant and tangent loss are plotted as a function of calcination temperature in Figure 7.16 (a, b). For nanoparticles synthesized using Sol-A dielectric constant decreases from 47.2 to 42.2 (log f =5.0) with increase in calcination temperature (Figure 7.16(a)). For nanoparticles synthesized using Sol-B dielectric constant decreases from 45.5 to 44.3 (log f =5.0). For nanoparticles synthesized using Sol-C dielectric constant increases from 95.5 to 107.5 (log f =5.0) with increase in calcination temperature from 300°C to 500°C. As calcination temperature was further increased to 900°C decrease in dielectric constant to 101.3 (log f =5.0) was observed. Increase in dielectric constant at calcination temperature 500°C is due to decrease in grain size to 18nm as was observed in SEM images of Figure 7.8(b). Reduction in grain size results in increase in number of grain boundaries. Electrons that hop through the conducting grain boundaries pile up at grain boundaries. Due to small grain size large number of electrons pile up at grain boundaries thus increasing the resistance of grain boundaries (Barsoukov and Macdonald 2005; El Hiti 1999; Majid et al. 2015; Riaz et al. 2015). This results in increase in dielectric constant and tangent loss at calcination temperature of 500°C. Further increase in calcination temperature resulted in increase in grain size (Figure 7.10(c, d)) thus resulting in increase of dielectric constant. In addition, it can be seen that iron oxide nanoparticles prepared using Sol-C resulted in high dielectric constant and low tangent loss as compared to nanoparticles prepared...
using Sol-A and B. High dielectric constant of iron oxide nanoparticles synthesized with Sol-C is due to phase purity of Fe$_3$O$_4$ as was observed in Figure 7.5(b). In addition, it was observed in Figures 7.8-7.10 that grain size of nanoparticles synthesized with Sol-C was less than that synthesized using Sol-A and B. Reduced grain size for nanoparticles prepared with Sol-C results in increased dielectric constant.

![Figure 7.16: (a) Dielectric constant and (b) Tangent loss for iron oxide nanoparticles plotted as a function of calcination temperature at log f = 5.0.](image)

For determination of grain and grain boundary resistance Cole-Cole plots for iron oxide nanoparticles synthesized with Sol-C can be seen in Figure 7.17. Ideally, three semicircles are present in Col-Cole plots indicating contribution from grain resistance, grain boundary resistance and interface resistance. However, only one semicircle was observed in Figure 7.17 due to high grain boundary resistance (Barsoukov and Macdonald 2005).

![Figure 7.17: Cole-Cole plot for iron oxide nanoparticles prepared with Sol-C.](image)
Cole-Cole plots in Figure 7.17 were fitted using Zview software with model composed of grain resistance connected in series with grain boundary resistance and capacitance. Results of Zview fitting are listed in Table 7.2.

**TABLE 7.2: Zview fitting parameters for iron oxide nanoparticles synthesized with Sol-C**

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>( R_g ) (Ω)</th>
<th>( R_{gb} ) (kΩ)</th>
<th>( C_{gb} ) (pF)</th>
<th>Relaxation frequency (kHz)</th>
<th>Relaxation time (μsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>112.3</td>
<td>178.9260</td>
<td>0.023941261</td>
<td>37.15352</td>
<td>4.283714</td>
</tr>
<tr>
<td>500</td>
<td>126.5</td>
<td>199.820</td>
<td>0.030987143</td>
<td>25.70396</td>
<td>6.191851</td>
</tr>
<tr>
<td>700</td>
<td>443.6</td>
<td>155.335</td>
<td>0.022937767</td>
<td>44.66836</td>
<td>3.563038</td>
</tr>
<tr>
<td>900</td>
<td>354</td>
<td>811.453</td>
<td>0.003487845</td>
<td>56.23413</td>
<td>2.830222</td>
</tr>
</tbody>
</table>

**7.4 Summary**

Iron oxide nanoparticles were prepared using sol-gel method with variation in concentration of oleic acid. Concentration of oleic acid was varied as 5%, 10% and 15% by volume. Sol prepared with high concentration of oleic acid showed superparamagnetic behavior while sols prepared with 5% and 10% by volume oleic acid showed mixed magnetic behavior. This mixed magnetic behavior of sols leads to presence of mixed phases of iron oxide. Pure magnetite phase was obtained with 15% by volume oleic acid. Calcination of nanoparticles from 300°C to 500°C strengthened magnetite phase indicated by increase in saturation magnetization. SEM images indicated the formation of nanoparticles with size ~18nm at 500°C. Best structural and magnetic properties of iron oxide nanoparticles with superparamagnetic behavior were obtained using 15% by volume oleic acid along with calcination of NPs at 500°C. Dielectric constant of ~107.5 (log f = 5.0) was observed for nanoparticles calcined at 500°C and synthesized using 15% by volume oleic acid due to high grain boundary resistance ~199.8kΩ.
CHAPTER-8
Chapter – 8  

FeO added ZnO Nanostructures

8.1 Introduction

Multi-functional and environment-friendly ZnO is one of the most important n-type II-VI semiconductor materials which attracted a lot of scientific interest because of its unique properties like wide direct band gap (3.37 eV) which makes this a strong candidate for optoelectronics and large exciton binding energy (60 meV) which helps in excitonic recombination for lasing mechanism even at room temperature (Arya et al. 2012; Kumar and Kim 2012).

Depending on crystal structure and various unique properties ZnO with the doping of transition metals also shows many important properties of diluted magnetic semiconductors and these diluted magnetic semiconductors can be used in various new generation spintronic devices like spin valve transistors due to the involvement of both charge and spin of the carriers (Sharma et al. 2009). ZnO has also found its potential applications in many fields like in paints (Ramezanzadeh et al. 2010), rubbers (Sim et al. 2005), cosmetics (Lewicka et al. 2011), bio and gas sensors (Chen et al. 2011; Zhao et al. 2013) and solar cells (Ding et al. 2007; Ko et al. 2011).

One of the most significant features of ZnO is low toxicity and biodegradability when used in nano dimensions. Zn$^{2+}$ is a vital trace element for adults; adult human being requires 7.0 to 9.5 mg of Zn$^{2+}$ per day. ZnO surface is chemically terminated by-OH groups; the surface of ZnO is mostly terminated by -OH groups, which can be easily functionalized by surface decorating molecules (He et al. 2010). ZnO can slowly dissolve in both strong basic and acidic conditions with direct contact to that solution (Zhou et al. 2006). All these properties make ZnO excellent candidates as biocompatible and biodegradable material for use in various biomedical applications such as bio-imaging and magnetic resonance imaging (Yim et al. 2011; Zhang and Liu 2010).

Besides all the benefits major difficulties for biomedical applications of ZnO nanomaterials include precise control on size and morphology of nanostructure along with stiffness and production of reactive oxygen species (ROS). This generation of (ROS) can lead to cell death when the antioxidative capacity of the cell is surpassed. Generation of ROS is related to the semiconducting nature of ZnO. In order to overcome these difficulties by tailoring nanoparticle size and morphology, it is possible to take the utmost benefit of the EPR/enhanced permeation and retention effect and doping of ZnO with transition metal. Transition metal doping enhances
the generation of ROS by potentiating redox-cycling cascades due to its catalytic behavior (Rasmussen et al. 2010). Among these transition metals doping of iron in ZnO is widely reported due to its various advantages like it is postulated that incorporation of Fe$^{+3}$ into the ZnO crystal lattice enhances the particle’s ability to generate ROS (Franco and Alves 2013). Iron being biocompatible reduces toxicity for mammalian cells along with large saturation magnetization which allows high magnetic moments (George et al. 2009; Kothiyal et al. 2010; Schneider et al. 2011; Soumahoro et al. 2010; Xia et al. 2011).

Among the synthesis methods we chose sol-gel method due to its various advantages like controlled particle size, low cost and vacuum free method. It also gives high compositional homogeneity (Bilecka et al. 2011). Moreover, it is easy to realize the dopant incorporation using a one-route process simply by modulating the ingredient of the precursors (Aydin et al. 2013; Liu et al. 2009a).

8.2 Experimental Details

Simple, economic and low temperature sol-gel method was used to synthesize iron doped ZnO nanoparticles with variation in dopant concentration as 1wt%, 2wt%, 3wt%, 4wt% and 5wt%. Research grade zinc acetate [Zn(CH$_3$COO)$_2$.2H$_2$O], and iron chloride [FeCl$_3$. 6 H$_2$O] were used as precursors. For preparation of un-doped ZnO sols two solutions (solution 1 and solution 2) were prepared prior to the final sol. Solution 1 was prepared by dissolving zinc acetate in DI water. The solution was stirred at room temperature. Solution 2 was prepared by dissolving triethyl amine (TEA) in isopropyl alcohol (IPA). The two solutions were mixed together and refluxed at 60$^\circ$C. Iron oxide sol was synthesized using iron chloride as precursor that was dissolved in mixture of ethanol and water. Appropriate amount of iron oxide sol was added drop wise to the ZnO sol under constant stirring to obtain iron doped Zn$_{1-x}$Fe$_x$O sol where $x=0.0-0.1$ (with interval of 0.01). Zn$_{1-x}$Fe$_x$O was then heated at 80$^\circ$C on a hotplate to obtain nanoparticles. The intermediate steps for the sol synthesis can be seen in Fig. 1. It is worth mentioning here that no gelation agent was used during the synthesis and the nanoparticles were prepared at low temperature of 80$^\circ$C and characterized without further calcination. The color variation of Fe doped ZnO sols and nanoparticles can be seen in Figures 8.1 and 8.2, respectively.

By sol-gel process inorganic products were obtained by the chemical reaction of precursors. The production of ZnO by sol-gel method generally involves hydrolysis of zinc acetate
Zn(CH₃COO)₂⋅2H₂O facilitated by TEA in isopropyl alcohol. The reaction involved for the synthesis is given in Equations 8.1 and 8.2 (Schneider et al. 2011).

\[
\begin{align*}
[Zn(CH₃COO)]^+ + H^+ + 2OH^- &\rightarrow CH₃COOH + Zn(OH)_2 \quad (8.1) \\
Zn(OH)_2 &\leftrightarrow ZnO + H₂O \quad (8.2)
\end{align*}
\]

The XRD patterns of as-synthesized iron doped ZnO were obtained by Bruker D8 Advance X-Ray diffractometer using Cu Kα radiation (λ=0.15406 nm). The surface morphology was characterized by Hitachi S3400N Scanning Electron Microscopy (SEM). Magnetic hysteresis loops of iron doped ZnO were measured by Lake Shore 7407 Vibrating Sample Magnetometer (VSM).

8.3 Results and Discussion

XRD patterns of pure and iron doped ZnO nanoparticles are shown in Figure 8.3. XRD spectra show diffraction peaks at angles of 20=31.631°, 34.501°, 36.251°, 47.501°, 56.601°, 62.801°,
66.361°, 67.921° and 68.911°, which are indexed as (100), (002), (101), (102), (110), (103), (112) and (201) diffraction lines showing wurtzite hexagonal structure of ZnO (JCPDS 36–1451) [Figure 8.3(a-f)]. Figure 8.3(a-e) reveals that, there is no change in the wurtzite structure of ZnO after Fe doping indicating that Fe atoms replace Zn atoms in the ZnO lattice till x=0.04. With further increase in dopant concentration peaks corresponding to α-Fe₂O₃ were observed.

![Figure 8.3: XRD patterns for iron doped ZnO NPs](image)

With further increase in iron concentration it can be seen that (Figure 8.3(f)) the XRD peaks of iron doped ZnO were broadened as compared with the peaks of pure ZnO. This broadening of peaks is due to two factors; one may be the smaller ionic size of Fe³⁺ (0.064nm) as compared to Zn²⁺ (0.072nm) (Wang et al. 2009). Due to this difference in ionic radii smaller crystallite size is observed with increase in doping as shown in Figure 8.4 (Ba-Abbad et al. 2013). Second factor can be doping of Fe into ZnO crystal lattice which prevents crystallization (Liu et al. 2009a) and hence low crystallinity was observed and small peaks of iron oxide (JCPDS 39-1346) were observed with increase in doping concentration to x=0.05. The low crystallinity of the nanoparticles with increasing Fe doping arises due to distortion in the host lattice that arises due to introduction of foreign atom (Fe) in the host lattice. This causes decrease in nucleation and increase in growth rate with increasing Fe dopant (Sharma et al. 2009) leading to decrease in crystallite size from 32nm to 19nm.
The lattice parameters $a$ and $c$ of hexagonal wurtzite ZnO as shown in Table 8.1, are also calculated by using Equation 8.3.

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{(h^2 + hk + k^2)}{a^2} \right] + \frac{l^2}{c^2} \quad (8.3)$$

It was observed that with the increase in iron doping lattice parameters decrease thus decreasing $c/a$ ratio as shown in Table 8.1. This decrease is due to smaller ionic radii of $\text{Fe}^{3+}$ as compared to $\text{Zn}^{2+}$ (Ba-Abbad et al. 2013).

Unit cell volume was also calculated by using Equation (8.4) below:

$$V = 0.886c^2a \quad (8.4)$$

The calculated unit cell volume given in Table 8.1 also shows that there is decrease in unit cell volume with increase in iron content. This is also due to smaller ionic size of $\text{Fe}^{3+}$ [41].

Fourier transform infrared (FTIR) spectra of pure and iron doped ZnO in the range of 2000–400 cm$^{-1}$ is displayed in Figure 8.5. For pure ZnO, the band at 466 cm$^{-1}$ is vibration mode, the wavenumber of this vibrational mode increases with increase in the Fe concentration from 466 to 474 cm$^{-1}$. The shift in the band position is due to the difference in the ionic radii between $\text{Zn}^{2+}$ and $\text{Fe}^{3+}$ (Pandiyarajan et al. 2012).
TABLE 8.1: Structural properties of iron doped ZnO NPs

<table>
<thead>
<tr>
<th>Dopant Concentration (%)</th>
<th>c(nm)</th>
<th>a(nm)</th>
<th>c/a</th>
<th>V (nm)$^3$</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.2099</td>
<td>3.246</td>
<td>1.605022</td>
<td>4.615971</td>
<td>32</td>
</tr>
<tr>
<td>1</td>
<td>5.2081</td>
<td>3.2466</td>
<td>1.604171</td>
<td>4.614377</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>5.2073</td>
<td>3.2469</td>
<td>1.603776</td>
<td>4.613668</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>5.2069</td>
<td>3.247</td>
<td>1.603603</td>
<td>4.613313</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>5.2062</td>
<td>3.2472</td>
<td>1.603289</td>
<td>4.612693</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>5.206</td>
<td>3.2475</td>
<td>1.603079</td>
<td>4.612516</td>
<td>19</td>
</tr>
</tbody>
</table>

Absorption bands at 1021 and 1112 cm$^{-1}$ are due to C-H stretching vibrational modes (Sharma et al. 2009). The absorption bands centered at about 1404 and 1583 cm$^{-1}$ can be assigned to the asymmetric and symmetric C=O stretching modes, respectively (Liu et al. 2009a). The bands centered at 620 cm$^{-1}$ to 678 cm$^{-1}$ are given by surface phonon modes. Surface phonon modes (SPM) normally appear as the particle size falls below incident IR wavelength (Pandiyarajan et al. 2012). The interaction between particle and the electromagnetic radiation depends on shape, size and lattice distortion (Pandiyarajan et al. 2012).

Figure 8.5: FTIR spectra of iron doped ZnO NPs.
Figure 8.6 shows transmission spectrum of Fe doped ZnO sols prepared with variation of doping concentration. The sols are highly transmitting in the visible and infrared region. Fe doped ZnO sols prepared at x=0.04 doping concentration have highest transmission as compared with the samples prepared with 0.00, 0.01, 0.02, 0.03 and 0.05. From the above results, it can be seen that iron doped ZnO sols have high transmittance in the visible and infrared range so the nanoparticles prepared using these sols can be used as window layer in optoelectronic devices [31].

The transmission properties are observed to be improved for Fe doped ZnO sols with increased doping concentration up to 0.04. This indicates that at doping concentration of 0.04 the size of colloidal suspension will be small thus leading to smaller particle size. Due to Quantum confinement effect, in these smaller nanoparticles, surface to volume ratio increases that plays important role to increase the transmittance of ZnO nanoparticles (Baranowska-Korczyc et al. 2012). ZnO sols prepared using Fe doping show transmission of greater than 80%. The transmission spectra that are shown in Fig. 6 are the transmission of ZnO sols prepared using microwave assisted sol-gel method. It is important mentioning it here that to the best of our knowledge there are so far no reports on studying the transmission spectra of the sols.

![Figure 8.6: Transmission curves for iron doped ZnO NPs.](image)

Large band gap materials are getting interest for optoelectronics at room temperature (Baranowska-Korczyc et al. 2012). The optical band gap energy of zinc oxide nanoparticles was calculated. The absorption coefficient was calculated using Equation (8.5).
\[
\alpha = \frac{1}{t} \ln \left[ 2 \frac{R^2T}{-(1 - R)^2 + \sqrt{(1 - R)^4 + 4R^2T^2}} \right]
\]  

(8.5)

Where “T” is transmittance of the zinc oxide nanoparticles deposited on glass substrate, “R” is the reflectance, and \( t \) is the film thickness.

The plots giving band gap energy estimation between \( \alpha^2 \) versus E(eV) in the UV–visible region are shown in Figure 8.7. The linear part of the plots has been extrapolated towards energy axis at \( \alpha=0 \). The intercept value on the energy axis has been found to be 3.41 eV in the case of sample prepared with doping concentration of 0.04. Variation in the band gap of the as-synthesized samples with the variation of doping concentration is shown in Figure 8.8.

Band gap of ZnO colloidal suspension obtained in the present work is observed to be slightly larger than that of bulk ZnO (3.37eV) (Ba-Abbad et al. 2013); it might be attributed to the smaller size. As the particle size decreases the band gap increases. Hence, the shift of absorption edge to the lower wavelength is observed which is mainly due to the quantum confinement effect (Ba-Abbad et al. 2013; Baranowska-Korczyc et al. 2012).

![Figure 8.7: (a) \( \alpha^2 \) vs. E(eV) plots (b) band gap as a function of dopant concentration for iron doped ZnO NPs.](image)

The magnetization (M) versus magnetic field (H) curves observed at different doping concentration is shown in Figure 8.8. Very slight variation in saturation magnetization and coercivity is observed as the dopant concentration is increased from 1-5wt% as can be seen in Figure 8.9. Table 8.2 shows comparison of saturation magnetization of un-doped and Fe doped ZnO prepared by sol-gel method. Fe doped ZnO nanoparticles show high saturation magnetization as compared to un-doped ZnO. It is important to mention it here that these
magnetic properties are much enhanced as compared to literature reported values as can be seen in Table 8.2. As magnetic dopant atom is incorporated in the non-magnetic host lattice the dopant atom generates local electric potential. This electric potential then gives rise to spatially distributed response. For small concentration of ions each dopant ion produces magnetic field around itself. This magnetic field then acts on other ions around itself. The result of which is the long range oscillating interaction between free carriers. This is known as RKKY interactions (Ruderman–Kittel–Kasuya–Yoshida) (Liu et al. 2009a). This ferromagnetic property, of low temperature synthesized, iron doped ZnO can be used in various biomedical applications for drug delivery by applying magnetic failed (Rozhkova et al. 2009).

![Figure 8.8: M-H curves for iron doped ZnO NPs.](image)

![Figure 8.9: Saturation magnetization and coercivity as a function of dopant concentration.](image)
Table 8.2: Comparison of magnetic properties of iron doped ZnO NPs with literature

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Un-doped ZnO</th>
<th>Fe doped ZnO</th>
<th>Ms (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms</td>
<td>Dopant concentration</td>
<td>Ms (emu/g)</td>
</tr>
<tr>
<td></td>
<td>(emu/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un-doped ZnO [38]</td>
<td>0.0676</td>
<td>1%</td>
<td>0.0887</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2%</td>
<td>0.0889</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3%</td>
<td>0.0891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4%</td>
<td>0.0893</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5%</td>
<td>0.0910</td>
</tr>
<tr>
<td>Fe doping (20%)</td>
<td></td>
<td></td>
<td>0.0910</td>
</tr>
</tbody>
</table>

We have investigated the effect of iron doping on the structural and magnetic properties in Zn$_{1-x}$Fe$_x$O grown by simple and cost effective sol–gel process. The dopant concentration was varied between 0-10wt%. These nanoparticles were synthesized at low temperature of 80°C and were characterized without further calcination. Slight shift of peak positions to higher diffraction angles in XRD indicated that the dopant was successfully incorporated in the host lattice. As the dopant concentration was increased to 5% diffraction peaks corresponding to iron oxide phase emerged thus distorting the crystal structure of ZnO. The magnetic properties of Zn$_{1-x}$Fe$_x$O showed the presence of a ferromagnetic behavior at room temperature. The observed ferromagnetism in Zn$_{1-x}$Fe$_x$O is due incorporation of Fe in the ZnO lattice as the result of long range oscillating interaction between free carriers. The presence of ferromagnetism in Fe-doped ZnO nanoparticles produced by simple sol–gel technique opens a new possibility in biomedical applications. The work presented in this thesis sets the groundwork for expanding the application of iron doped ZnO nanostructures in bioscience.
CHAPTER-9
Chapter – 9  Mn/Fe Co-doped ZnO Nanostructures

9.1 Introduction

Diluted magnetic semiconductors (DMSs) have gained much interest in the field of optoelectronic devices and spintronics due to the involvement of both charge and spin of electrons (Fan et al. 2012; Lin et al. 2013; Wang et al. 2013a). Zinc oxide is one of the promising materials to obtain DMS due to its wide band gap at room temperature, i.e., 3.37 eV and large exciton binding energy i.e., 60 meV. Doping of much smaller amount of transition metals [Mn(Anghel et al. 2010), Fe(Lin et al. 2013), Co(Kang et al. 2013), In(Jiao et al. 2011), V(Hong et al. 2005), and Cr(Liu et al. 2009b)] plays an important role in the structural and magnetic properties of zinc oxide to act as DMS. Compatibility of Mn in ZnO is because of its close resemblance of ionic radii with Zn along with its thermal solubility. Mn has electron effective mass ~ 0.3m_e (m_e is free electron mass), which results in large injected spins and charge carriers making Mn:ZnO useful for the spintronic nanodevices (Sharma et al. 2003). Fe is also one of the important candidates for doping to obtain the DMS. Goktas et al. reported the influence of Fe doping on ZnO thin films deposited by sol-gel spin coating method in order to observe the room temperature magnetism. Co-doping of various transition metals plays an important role in the improvement of structural, optical, and magnetic properties of DMSs (Goktas et al. 2013a; Sharma and Jha 2017). Chakrabarti et al. reported room temperature ferromagnetism in Mn/Fe co-doped ZnO by solid state reaction method and found that the co-doping of Mn/Fe improved magnetic properties as compared to un-doped materials (Chakrabarti et al. 2008). Xu et al. reported the synthesis of Cu and Co co-doped ZnO using sol-gel method in order to investigate the effect of shape and hydrogenation on magnetic properties of synthesized nanopowder (Xu et al. 2009).

Un-doped and doped ZnO thin films have been prepared by different techniques such as pulsed laser technique (Fan et al. 2012), chemical vapor deposition (Chang et al. 2011), co-precipitation method (Saleh et al. 2013), RF magnetron sputtering (Singh and Venkaiah 2012), and sol-gel method (Goktas et al. 2013b; Riaz et al. 2011).

In this chapter, we report synthesis of Mn/Fe co-doped ZnO sol using sol-gel method. Thin films were achieved by spin coating onto suitable substrates (glass and copper) to achieve multilayered effect. To the best of our knowledge, there are no reports on Mn/Fe co-doped ZnO thin films by
sol-gel method to date. Effect of co-doping of Mn and Fe on structural and magnetic properties of ZnO was studied.

9.2 Experimental Details

Sol-gel method is used for the synthesis of un-doped and Mn/Fe co-doped ZnO sols. Zinc acetate bi-hydrate [Zn(CH₃COO)₂.2H₂O], iron nitrate non-hydrate [Fe(NO₃)₃.9H₂O] and manganese(II) acetate tetra-hydrate [C₄H₆MnO₄.4H₂O] were used as precursors, whereas IPA, TEA, and ethylene glycol were used as solvents. In the first step, ZnO sol was synthesized. In the second step, Mn doped ZnO sols were synthesized. In the third step, for the Mn/Fe co-doped ZnO, three solutions were prepared in order to get the final Mn/Fe co-doped ZnO sols. Dopant concentration was varied in the range of 1wt% to 5wt%. The 1:1 molar ratio of Mn and Fe was used. MnFeO sol was synthesized by dissolving 0.245g C₄H₆MnO₄.4H₂O and Fe(NO₃)₃.9H₂O in ethylene glycol under constant magnetic stirring for 1 h. Mn/Fe co-doped ZnO sol was obtained by drop wise addition of dopant sol in freshly prepared ZnO sol.

Co-doped sols were stirred continuously at room temperature for 4 h. Transparent sols were obtained for doping concentration up to 4wt%. However, the colorless transparent sol changed to greyish black transparent color with the increase in doping concentration to 5wt%. Mn/Fe co-doped ZnO sols were spin coated on cleaned glass and copper substrates at 3000 r/min for 30 s, followed by magnetic field annealing at 300˚C for 1 h. Crystalline structure and phase of the films was observed using Rigaku D/Max II-A X-ray Diffractometer (XRD) with CuKα (λ=1.5405Å). Diffraction angle was adjusted from 20˚ to 80˚ with step width of 0.02˚. Lakeshore 7407 vibrating sample magnetometer was used to study hysteresis loop of the samples. Hitachi S-3400N scanning electron microscope was used to investigate the surface morphology of doped films.

9.3 Results and Discussion

9.3.1 Structural characterization

Figure 9.1 shows XRD pattern of 5wt% Mn-doped ZnO. It was observed that up to 5wt% doping of Mn, there are no structural changes in ZnO wurtzite structure and no peak corresponding to Mn₂O₃ was observed. Absence of dopant oxide and metals’ diffraction peaks in Fig. 9.1 indicates that Mn has successfully replaced Zn in the host lattice hence forming DMS (Peng et al. 2005). Wurtzite structure is non-centrosymmetric and hence more favorable for inducing and studying
magnetism in this material. Mn concentration incorporated into ZnO lattice was estimated to be ~2.6% by following Vegard’s law for 5wt% doped ZnO. Solid solubility limit of Mn in ZnO matrix is about 13% (Jiang et al. 2011) that is why Mn concentration of 5wt% (nominal composition) is too low to cause change in the wurtzite structure of ZnO.

Figure 9.1: XRD pattern of Mn doped ZnO.

XRD patterns of un-doped and Mn/Fe co-doped ZnO are shown in Figure 9.2. Presence of high intensity peaks (100), (002), and (101) gives clear evidence of the formation of hexagonal wurtzite structure of ZnO. XRD results show that co-doping up to 4wt% [Figure 9.2(b)] did not change the hexagonal wurtzite crystal structure. However, as the dopant concentration was increased to 5wt%, small diffraction peaks corresponding to Mn/Fe$_2$O$_3$ (JCPDS card no. 32-0637 and 39-1346) respectively) are observed as shown in Figure 9.2(c).

The average crystallite size (D) calculated from the XRD data using Scherer formula is in the range of 12 to 19 nm with the variation in dopant concentrations.

Figure 9.2: XRD graphs of (a) un-doped, (b) 4wt% and (c) 5wt% Mn/Fe co-doped ZnO nanostructures based thin films (*Mn/Fe$_2$O$_3$).
9.3.2 Surface Morphology

Figure 9.3 shows SEM images of Mn/Fe co-doped ZnO nanostructured thin films. It is clearly observed from Figure 9.3 that average grain size decreases with increase in doping concentration of the Mn/Fe. These results are consistent with the XRD analysis of samples. Grains are uniformly distributed throughout the surface and slight variation in size and shape of grains is attributed to the ionic radii of dopants. Low radii of iron and manganese as compared to Zn resulted in decrease in the grain size. It is clear from the SEM micrographs that uniform distribution is observed for samples with very fine grains in the case of 1-4wt% Mn/Fe co-doping. Chikoidze *et al.* observed grains with a diameter of 100-130nm in the case of Fe and Ni-doped nanostructured thin films. Mn/Fe co-doping concentration has a significant influence on morphology of ZnO film (Chikoidze *et al.* 2013).
Crystallite size decreased (16 to 12nm) with the increase in concentration of dopant elements up to 4wt%. Decrease in crystallite size might have been observed because of smaller ionic radii of manganese and iron as compared to zinc. This can be observed from increment in full-width at half maximum (FWHM) of the XRD peaks as the dopant’s concentration increased. However, increase in crystallite size up to 19 nm was observed with the further increase in dopant concentration to 5wt%. Slight shifting of peaks for Mn/Fe co-doped sample, towards lower angle is due to stresses present in the film. As the number of dopant atoms increases at the substitution sites, stresses due to difference in ionic radii of dopants and host lattice atoms are produced (Balamurali et al. 2013). The shift in peak positions with increase in Mn/Fe doping concentration indicates the expansion of the lattice parameters (Balamurali et al. 2013).

Doping concentration not only has a tremendous effect on grain sizes, but also on their shape. ZnO films with 1wt% dopants concentration show the formation of nanorods with diameter of 80nm and length of 200 nm. By increasing dopant concentration to 2wt%, nanostructure changed from nanorods to nanospheres with a diameter of 150 nm [Figure 9.3(b)]. The size of nanostructure further reduced to 100 nm by increasing the dopants to 4wt% as shown in Figures 3.9(c) and (d). This might be due to the fact that Mn and Fe ions could affect the ZnO crystal lattice at nano-scale and alter the preference of the crystal growth from rod-like to nanospheres. By increasing the dopant concentration to 5wt% agglomeration occurred, as shown in Figure 9.3(e), due to which magnetization value also reduced as shown by the VSM results in section 9.3.3.
9.3.3 Magnetic Characterization

Figure 9.4 shows hysteresis of Mn-doped ZnO with ferromagnetic nature. It was observed that the squareness and magnetization of samples increased with increase in Mn content in the range of 1 to 5wt% (M1–M5). High squareness of ferromagnetic behavior can be employed in switching operation for spintronic devices (Chang et al. 2011; Wang et al. 2013a).

Figure 9.4: Hysteresis loop of 5wt% Mn doped ZnO. Inset: hysteresis loop of 1-5wt% Mn doped ZnO.

Figure 9.5 shows multilayered structure like hysteresis of Mn/Fe co-doped ZnO. Wu et al. reported similar results by deposition of stacked layers of different magnetic oxides (Wu et al. 2013). However, such results are observed in the present study by simple co-doping of transition metals using sol-gel technique.

Figure 9.5: Hysteresis loops of Mn/Fe co-doped ZnO nanostructured thin films at various doping concentration. Inset: hysteresis loop indicates presence of multilayered like structure formed by co-doping of Mn and Fe ions in ZnO for 3wt% Mn/Fe co-doping.
The saturation magnetization increased with the increase in dopant concentration from 1 to 3wt%. Saturation magnetization and squareness is plotted as a function of doping concentration in Figure 9.6. Coupled magnetic moments of dopant atoms (Mn/Fe) has lowered the formation energy for Zn vacancies and enhanced ferromagnetic behaviour (Fan et al. 2012).

![Figure 9.6: Saturation magnetization and squareness versus dopant concentration.](image)

Hole-mediated exchange interactions are also responsible for ferromagnetic behavior due to introduction of hole by the exchange of Fe$^{3+}$ ions with Zn site in Fe doped ZnO.

Charge transfer in mixed valance electrons was predicted as origin of ferromagnetism in Co/Fe co-doped ZnO (Beltrán et al. 2013). It can be related to multilayered structure where during charge transfer an additional charge from the dopant results in magnetoelectronic coupling, which results in layering structures (Balamurali et al. 2013) as was observed in Figure 9.5.

In the present study, Mn/Fe co-doped ZnO samples showed much stronger ferromagnetic behaviour as compared to that reported in literature (Fan et al. 2012) where co-doped films were prepared using PLD after mixing and annealing (up to 800°C for several hours) the powders by solid state reaction; comparison is given in Table 9.1.

There are many possible origins for the presence of ferromagnetism in the multilayered structures. First reason is the formation of the secondary phases (Singh and Venkaiah 2012), but this option can be easily ruled out as XRD [Figure 9.2] showed that there were no peaks of the secondary phase. Second possibility is the presence of diffraction peaks corresponding to metals (Singh and Venkaiah 2012) since Mn and/or Fe both can be the dominant source of the
ferromagnetism, but again XRD results clearly showed the absence of metal diffraction peaks up to dopant concentration of 4wt%.

TABLE 9.1: Comparison of saturation magnetization of un-doped, doped and co-doped ZnO nanostructure based thin films

<table>
<thead>
<tr>
<th>Un-doped (Riaz et al. 2011)</th>
<th>Mn-doped</th>
<th>Mn/Fe co-doped (Balamurali et al. 2013)</th>
<th>Mn-doped (Fan et al. 2012)</th>
<th>Mn/Fe co-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mₘ (emu/gm) (wt%)</td>
<td>Mₛ (emu/gm) (wt%)</td>
<td>Mₛ (emu/gm)</td>
<td>Mₛ (emu/gm)</td>
<td>Mₛ (emu/gm)</td>
</tr>
<tr>
<td>5.16</td>
<td>1.66</td>
<td>1</td>
<td>5.16</td>
<td>3.5E-5</td>
</tr>
<tr>
<td>2</td>
<td>1.66</td>
<td>2</td>
<td>5.52</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>2.65</td>
<td>3</td>
<td>5.73</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.73</td>
<td>4</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.97</td>
<td>5</td>
<td>4.99</td>
<td></td>
</tr>
</tbody>
</table>

Now, the third reason for ferromagnetic behaviour is RKKY interaction between conductive electrons of ZnO and spin polarized electrons of Mn²⁺ and Fe³⁺ ions in case of Mn/Fe co-doped ZnO nanostructures. Such interactions can appear because of the spin polarization of conductive electrons in the ZnO host lattice. In addition, after the exchange interaction with local spin polarized electrons of Mn and Fe ions these local spin polarized electrons exhibit same spin direction as conductive electrons after long range exchange interaction. Thus, due to this exchange interaction material shows ferromagnetic properties (Zak et al. 2011).

Another strong reason, reported previously (Riaz et al. 2011) in the case of room-temperature ferromagnetism in un-doped ZnO is the presence of Zn vacancies. Table 9.1 shows the comparison of Mₛ values of un-doped, Mn-doped and Mn/Fe co-doped ZnO nanostructured thin films prepared by sol-gel and spin coating method. It can be seen in Table 9.1 that Mn and Fe co-doped ZnO shows high saturation magnetization as compared to the un-doped and Mn-doped...
ZnO. It is important to mention here that these magnetic properties are much enhanced as compared with those reported in the literature.

9.4 Summary

Nanostructured thin films of Mn/Fe co-doped ZnO were successfully prepared by simple and economic sol-gel and spin coating method. Dopant concentration of Mn/Fe was varied in the range 1-5 wt%. XRD data showed the incorporation of transition metal ions without formation of oxides of dopants up to 4wt%. SEM results indicated the formation of nanorods at 1wt% of Mn/Fe co-doping in ZnO thin films. Increase in dopant concentration not only affected the shape from rods to spherical, but also has varied the grain size. Material showed magnetic hysteresis with high saturation magnetization for 3wt% Mn/Fe co-doping. Shape of M-H curves is similar to that of multilayered structure indicating that such complex structures can be replaced by a single ZnO layer with co-doping of Mn and Fe.
CHAPTER-10
10.1 Introduction

Density functional theory was used to investigate structural, optical and magnetic properties of the iron oxide nanostructure. Amsterdam density functional (ADF) program (details are given in second chapter) with 2014.05 package was used. Computational details carrying detail of the input parameters used for the investigation of above-mentioned properties of wüstite, hematite, maghemite and magnetite are given in this chapter. Computational details used for theoretical investigation of various properties, like structural, electronic optical and magnetic, are given below.

10.2 Theoretical Investigation of Wüstite (FeO)

Being the member of transition metal (TM) monoxides, FeO has strongly correlated electron systems. In the narrow 3d bands of transition metals, interaction between delocalized and localized effects results different electronic structure of FeO (Schrettle et al. 2012). Large number of experimental and theoretical studies has been carried out to investigate properties of transition metal monoxides but only few reports are present about wüstite (Gillen and Robertson 2013). Wüstite has been less investigated due to its non-stoichiometric existence at room temperature. Cubic wüstite, (Fe_{1-x}O), can only be synthesized at ambient pressure with variation of x in the range of 0.05 < x < 0.15 (Schrettle et al. 2012). While, meta-stable wüstite gives mixture of two phases of iron oxide: one is hematite while second is magnetite (Schrettle et al. 2012).

It possesses stable cubic NaCl (B1) like crystal structure under ambient temperature and pressure (Eom et al. 2014; Fischer et al. 2011). Face centered cubic unit cell is formed with oxygen (O^2-) lattice and Fe^{2+} substitutes on interstitial sites (Benitez et al. 2011). With variation in temperature and pressure structure deformation is observed such as at room temperature and high pressure of 17GPa monoclinic crystal structure is observed (Fischer et al. 2011). Above room temperature and at high pressure of about 70GPa or above it, transformation from B1 to B8 (NaCl to NiAs) and B2 (CsCl) crystal structure is observed (Eom et al. 2014; Kaercher et al. 2012), that belongs to Fm\overline{3}m space group (Schrettle et al. 2012).
10.3 Computational Details to Investigate Properties of wüstite by ADF

Density functional theory was used to theoretically investigate structural, electronic, optical and magnetic properties of wüstite at 0K. BAND program in Amsterdam density functional (ADF) package was used for all unrestricted calculations.

In the first step crystal structure was constructed by using space group selection in BAND code. In order to use this option we first select the space group i.e. in case of wüstite we selected Fm$\overline{3}$m space group, as wüstite exists in rock salt i.e. NaCl type crystal structure (Schrettle et al. 2012). After the selection of space group, lattice parameter was inserted. In the next step atomic positional parameters were selected and unit cell of wüstite was constructed. Atomic positional parameters used for the geometry optimization of wüstite are given in Table 10.1 (Fjellvåg et al. 2002).

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (Fe)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

To get the stable crystal structure, geometry optimization was performed in BAND code. Slight variation in lattice parameter was done to get the geometry convergence with lowest value of formation energy. This variation was done because in literature different values of lattice parameters were quoted like Wdowik et al. (2015) used lattice constant “a” with a value of 4.35 Å to theoretically investigate electronic and dielectric properties of the wüstite while Ta et al. (2015) reported the use of 4.347 Å as lattice constant in theoretical investigation of various absorption properties of wüstite (Ta et al. 2015; Wdowik et al. 2015). Beside these theoretically calculated values of lattice constants, 4.283Å, 4.333Å and 4.31Å are the experimentally reported values of lattice constant for wüstite (Batista et al. 2015; Yu et al. 2015). Therefore we wanted to find out the exact or most relevant value, which should be in good agreement to the experimentally reported value of lattice parameter of wüstite. It was observed that for a=4.33 Å, system gets the lowest formation energy per atom (-4.2964 eV) which indicated the stability of the structure. With the variation in lattice constant unit cell volume for each variation was calculated and formation energy verses unit cell volume was plotted as shown in Figure 10.1.
Hence, 4.33 Å was used for all calculations of wüstite.

![Figure 10.1: Formation energy verses unit cell volume curve for wüstite.](image)

In the next step, basis set was also optimized. As ADF program (version 2014.01) contains five different types of basis sets known as DZ, DZP, TZP, TZ2P and QZ4P. All these basis sets contain s, p, d and f type Slater type orbitals (Van Lenthe and Baerends 2003). DZ is the double zeta while DZP, TZP and TZ2P are triple zeta in the core. Whereas all-electron QZ4P is a basis set with quadruple zeta in the core (Van Lenthe and Baerends 2003). TZ2P was used as basis set for all unrestricted calculations after optimization. TZ2P, as described above, is triple zeta type basis set in all electrons and two sets of polarization functions were used to augment this basis set (Ma and Li 2015).

The two most widely used approximations i.e. local density approximation (LDA) and generalized gradient approximation (GGA) in BAND tool of ADF software were used here for the theoretical investigation of wüstite at 0K. In case of generalized gradient approximation (GGA), selection of exchange correlation potential was made by calculating structural and optical properties like band gap of wüstite. PBE (Perdew-Burke-Ernzerhof) was used for all calculations.

**10.4 Results and Discussion**

**10.4.1 Structural Properties**

Figure 10.2 shows cubic structure of wüstite by using Amsterdam density functional (ADF) software, which is the stable structure for wustite at ambient conditions (Fischer et al. 2011). Periodic unit cells containing three-layers were used for geometric optimization of the rock salt...
crystal structure of FeO at 0K. This is also known as B1 (NaCl) type crystal structure (Eom et al. 2014). Bond length, between iron and oxygen, of 2.2 Å was observed after geometry convergence for this cubic structure, which is in accordance to the reported value i.e. 2.16 Å (Ramimoghadam et al. 2014).

Figure 10.2: Structure of wüstite at 0K (Red atoms of Iron and blue ones are of oxygen atoms)

10.4.2 Band Structure and Density of States (DOS)

Band structure calculated by using LDA is plotted as given in Figure 10.3 (a) to (c). Whereas, band structures calculated by using GGA is plotted as given in Figure 10.4 (a), (b) and (c). Fermi level is at 0 for both LDA and GGA calculations and shown by the black dotted line at y=0. Spin up i.e. majority spin is represented by red color while blue color indicates spin down i.e. minority spins.
Figure 10.3: Band structure of wüstite calculated by LDA a) Combine spin-up and spin-down, b) for spin-up state and c) for spin-down state.
Figure 10.4: Band structure of wüstite calculated by GGA a) Combine spin-up and spin-down, b) for spin-up state and c) for spin-down state.

From Figures 10.3 (a) and 10.4 (a), it is observed that band gap for wüstite is zero which is a result of underestimation of electron-electron interaction of 3d electron of iron in wüstite (Wdowik et al. 2013). Same result is observed for both LDA and GGA at 0K, which shows metallic nature of wüstite (Eom et al. 2014).

Partial and total density of states for both LDA and GGA are plotted in Figure 10.5 (a) and (b) and Figure 10.6 (a) and (b), respectively that was investigated to observed magnetic nature and to confirm band gap of wüstite.

Figure 10.5: a) partial and b) total DOS by LDA.
Metallic nature for wüstite is observed for both LDA and GGA calculations since at ambient conditions insulating ground state fails to obtain by using simple approximations in DFT (Shorikov et al. 2010).

10.4.3 Inaccurate Results and Their Solution

Local density approximation (LDA) and generalized gradient approximation (GGA) are the most renowned and extensively used approximations in density functional theory. However, underestimation of band gap for transition metal oxides (TMO) is the main problem with both of these approximations. This underestimation is due to the deficiency of self-interaction cancelation and inappropriate description and correlation exchange in comparison to changes (Catlow 2003). In case of materials having transition metals, with d shells, this problem exceeds and may give wrong prediction of electronic structure of that material. For example GGA underestimates the experimentally observed band gap of iron oxide and gives 75% smaller value of band gap energy (Guo et al. 2012). In order to improve this underestimation of GGA and LDA for materials having transition metal, Hubbard potential (U eV) can be added. This leads to the GGA+U and LDA+U methods (Guo et al. 2012). Addition of Hubbard potential U in LDA and GGA is one of the modest approaches that were formulated, for the correlated systems, for improvement of explanation of the ground state. Due to low computational cost and simple expressions this Hubbard correction to approximate functionals (like LDA and GGA) in DFT has promptly become very widespread in the community of ab-initio calculation (Himmetoglu et al. 2014).

10.4.4 Optimization of Hubbard Potential (U)
Hubbard potential re-established band gap, by affecting ground state of the material, with usage of more precise explanation of electron-electron interactions in the band structure (Himmetoglu et al. 2014). Different values of Hubbard potential were reported by different researchers like Schron and Bechstedt (2013) reported the use of 4 eV as Hubbard potential for iron and Wang et al. (2013) reported the use of 3 eV as Hubbard potential (Schrön and Bechstedt 2013; Wang et al. 2013b). Torres et al. (2014) used U=3.5 eV for “d” electrons of iron (Torres et al. 2014).

Effect of Hubbard potential was investigated by varying the values from 0.1 to 1 eV and the band gap is plotted in Figure 10.7 for both LDA and GGA. Optimized value of 0.6 eV of Hubbard potential was used for final calculations of electronic structure and optical and magnetic properties of wüstite by GGA and LDA. All the computational results were taken at 0K.

\[ \text{Figure 10.7: Variation of the band gap with the applied Hubbard potential using the LDA and GGA.} \]

**10.4.5 LDA+U and GGA+U Calculations**

Figure 10.8 (a), (b) and (c) shows the band structures from our calculations using the LDA+U while in case of GGA+U, Figure 10.9 (a), (b) and (c) shows the calculated band structure for wüstite. Red color indicates majority spins (spin-up) and blue color indicates minority spins (spin-down) in Figures 10.8 (a-c) and 10.9 (a-c). According to crystal field theory, d band of iron is splitted in t_{2g} and e_{g} sub-bands, which are triply degenerated and doubly degenerated, respectively. Insulating ground state at ambient conditions fails to be obtained by using LDA. Hence, it shows metallic nature for all volumes (Shorikov et al. 2010).
Figure 10.8: Band structure of wüstite calculated by LDA+U; a) Combine spin-up and spin-down, b) for spin-up state and c) for spin-down state.
In all cases (GGA, GGA+U, LDA and LDA+U), the top of valence band consists of mixed 2p states of oxygen and inadequately dispersed d states of iron. Degenerate $e_g$ orbitals are formed by the splitting of five-fold degenerate d orbitals, and degenerate $t_{2g}$ orbitals are formed by three-fold degenerate orbitals as a result of octahedral crystal field splitting (Gillen and Robertson 2013).

The fundamental band gap is between 4s band and single band of $t_{2g}$ of iron (Gillen and Robertson 2013). Band gap of 2.08 eV and 2.34 eV is observed from Figures 10.9 (a) and 10.10 (a), after applying Hubbard potential of 0.6 eV to LDA and GGA, respectively. These values are given in Table 10.2 and can be seen that the band gap energy of 2.34 eV obtained in our calculations by using GGA+U, is in slightly better agreement with the experimental value i.e. 2.4 eV (Eom et al. 2014) by using GGA+U with Hubbard potential 0.6 eV.

**TABLE 10.2: Comparison of band gap values by using GGA, GGA+U, LDA and LDA+U (U=0.6 eV)**

<table>
<thead>
<tr>
<th>Used approximation in ADF</th>
<th>Used Exchange correlational potential</th>
<th>Applied Potential (eV)</th>
<th>Obtained band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our Calculations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADF (LDA)</td>
<td>CAPZ</td>
<td>0.6</td>
<td>2.08</td>
</tr>
<tr>
<td>ADF(GGA)</td>
<td>PBE</td>
<td>0.6</td>
<td>2.34</td>
</tr>
<tr>
<td>Literature</td>
<td>VASP (Toroker et al.)</td>
<td>PBE</td>
<td>6</td>
</tr>
<tr>
<td>Theoretical</td>
<td>2011)</td>
<td>PBE+U</td>
<td>4.2</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>----------------------------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>VASP (GGA) (Eom et al. 2014)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VASP (Wdowik et al. 2015)</td>
<td></td>
<td>PAW</td>
<td>5</td>
</tr>
<tr>
<td>VASP (Forti et al. 2012)</td>
<td></td>
<td>PAW</td>
<td>5</td>
</tr>
<tr>
<td>Literature Experimental (Eom et al. 2014)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 10.10](image1.png)

Figure 10.10 (a) and (b) shows partial and total density of states calculated by LDA+U while Figure 10.11 (a) and (b) shows for GGA+U calculations.

![Figure 10.11](image2.png)

Figure 10.10: a) partial and b) total DOS by LDA+U.
Electronic configuration of Fe in FeO is $3d^6$. Hence in FeO, high magnetization configuration is obtained due to division of d electrons in majority spin and minority spin. Normally five d electrons occupy majority spin state and remaining one occupies the minority spin states (Himmetoglu et al. 2014). Antiferromagnetic behavior of wüstite is observed from Figure 10.11 (b) and Figure 10.12 (b), which is in accordance to the experimentally obtained magnetic behavior of wüstite (Wdowik et al. 2015).

10.5 Summary

Density functional theory was used to investigate structural, optical and magnetic properties of iron oxide at 0K. BAND code was used in Amsterdam density functional software. Effect of Hubbard potential U (eV) on LDA and GGA approximations was investigated. Geometry optimization was achieved by using TZ2P as basis set along with PBE as exchange correlation potential. Calculation of lowest formation energy for iron oxide with lattice parameter 4.33Å was obtained for stable cubic crystal structure. Band structure for GGA and LDA calculations represent the metallic nature of iron oxide by underestimating the band gap of iron oxide. Partial and total density of states for these two calculations was also in agreement to the observed band structure. To get improved results, Hubbard potential was applied after optimization from 0.1 to 1 eV. With low value of Hubbard potential (0.6 eV) improved band gap of 2.34 and 2.08 was observed for GGA+U and LDA+U calculations, which is in good agreement to experimentally reported value of band gap for iron oxide. Antiferromagnetic behavior for GGA+U was also observed from obtained density of states. From these calculations it was observed that GGA+U gave more accurate results as compared to LDA+U. Hence, Amsterdam density functional (ADF)
program can be used to get improved electronic properties with relatively lower value of Hubbard potential in generalized gradient approximation which gives reproducible results in low computer cost.
CHAPTER-11
Chapter – 11  Theoretical Investigations – αFe₂O₃

11.1 Introduction

Different phases of iron oxide such as Fe₃O₄, α-Fe₂O₃ and γ-Fe₂O₃ with different structures constitute an outstanding category of functional materials that can be applied in various fields like biomedical and spintronic (Akbar et al. 2014b; Blanco-Andujar et al. 2015). Interest in iron oxide now focuses on control of their electric, magnetic, optic and dielectric properties (Tadic et al. 2014).

Among these research oriented phases of iron oxide, hematite (α-Fe₂O₃) on the basis of its natural abundance, electrochemical stability and band gap (2.1eV) has potential applications in photocatalytic water splitting (Chamberlin et al. 2015), catalytic process (Meng et al. 2013) and in various sensing applications such as in gas sensors (Cuong et al. 2012) and humidity sensors (Tulliani et al. 2013). Hematite is the thermodynamically most stable phase among different phases of iron oxide. It exists in corundum-type (alpha-Al₂O₃) structure under ambient conditions. It is the most common crystalline form, among different crystalline forms of iron oxide (Wanaguru et al. 2016). It is isostructural with cromia (α-Cr₂O₃) and corundum (α-Al₂O₃), and has been widely studied, both experimentally and by techniques based on atomistic simulation (Dzade et al. 2014). Some of the properties investigated by using Amsterdam density functional package are given here.

11.2 Computational Details for the Investigations of Properties of Hematite by ADF

Structural, electronic, optical and magnetic properties of hematite were investigated by using Amsterdam density functional (ADF) package. In the first step geometry optimization was carried out using BAND code by first selecting space group i.e. in case of hematite R̅3c (167) was used (Yu et al. 2015). Atomic positional parameters, given in Table 11.1, were used to construct unit cell for geometry optimization (Blake et al. 1966).

TABLE 11.1: Atomic positional parameters for Hematite

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (Fe)</td>
<td>12c</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Lattice parameters were selected after optimization and geometry convergence was achieved for \(a=b=5.035 \text{ Å}\) and \(c=13.75 \text{ Å}\) (Ramimoghadam et al. 2014). Figure 11.1 shows the obtained formation energy for unit cell volume calculated for each set of varied lattice parameters. Crystal structure of hematite was modeled using hexagonal unit cell comprising of six formula units (Dzade et al. 2014). Basis set, TZ2P, of plane-waves was employed in a periodic system for the solution of Kohn-Sham equations involved in density functional theory. Un-restricted calculations were calculated with widely used generalized gradient approximation (GGA). Perdew-Burke-Ernzerhof (PBE) was the form of functional used in the approximation. GGA+U approach with \(U=0.6 \text{ eV}\) was applied in order to correct electronic correlation of 3d electrons of iron. To the best of our knowledge it is the smallest value of \(U\) ever reported. Supercell was used to sample Brillouin zone and Band structure of hematite.

![Figure 11.1: Formation energy versus unit cell volume curve for hematite.](image)

**11.3 Results and Discussion**

**11.3.1 Structural Properties**

Figure 11.2 (a) and (b) shows crystal structure of super cell and unit cell of hematite, respectively. Hematite crystallizes in trigonal rhombohedral cells. Oxygen and iron atoms are arranged in trigonal hexagonal arrangement with lattice parameters \(a=b=5.035\text{Å}\) and \(c=13.75\text{Å}\) (Ramimoghadam et al. 2014). With this structure it belongs to the space group of R-3c (No. 167) along with formula units per unit cell=6 (Dzade et al. 2014). Lattice constants are also optimized to get lowest ground state energy for the stable structure of hematite after geometry optimization.
Energy stability of hematite with 12 atoms of iron was compared for different lattice parameters and it was observed that $a=b=5.035\text{Å}$ and $c=13.75\text{Å}$ were in good agreement with the experimentally observed values of lattice constants for stable hematite structure (Ramimoghadam et al. 2014). Bond angles after geometry optimization remained same as for hematite $\alpha=\beta=90$, $\gamma=120$.

![Crystal structure of hematite](image)

**Figure 11.2**: Crystal structure of hematite a) supercell and b) unit cell after geometry optimization by ADF. Color scheme O=red atoms and Fe=dark gray.

### 11.3.2 Band Structure and Density of States (DOS)

By using generalized gradient approximation in Amsterdam density function software, band structure for hematite was calculated and plotted as in Figure 11.3 (a), (b) and (c). Band structure for majority spin and minority spin states, is shown in Figure 11.3 (b) and (c), respectively.

![Band structure plots](image)
Figure 11.3: a) Band structure of hematite b) band structure for spin-up states and c) band structure for spin-down states, calculated by GGA.

Fermi level (shown by black dotted line) lies at zero for both spin-up and spin down states. From Figure 11.3 (a) it is clear that band gap calculated by GGA is zero. Partial and total density of states for hematite is given in Figure 11.4 (a) and (b) and is also in accordance with the band structure of hematite calculated by GGA.

Figure 11.4: a) partial DOS b) Total density of states of hematite calculated by GGA.

By using Generalized Gradient Approximation in density functional theory the calculated band gap does not result in accordance with the experimentally obtained band gap i.e. 2.1 (Tadic et al. 2014). This underestimation of band gap is because of strong electron-electron interaction in iron. Hence density functional theory fails to deal with strongly correlated systems such as for
hematite. To overcome this drawback of DFT, on-site potential is applied which is known as Hubbard potential (Chaudhury et al. 2014; Zhou et al. 2016).

11.3.3 Band Structure and Density of States (DOS) with Hubbard Potential

In order to get optimized value of Hubbard potential for hematite we have verified different values for Hubbard potential (U eV) and its effects on the band-gap of hematite is given in Figure 11.5.

From this it is observed that U = 0.6 eV results in a good explanation of the band-gap of different phases of iron oxide. Band structure obtained by applying this optimized Hubbard potential is given in Figure 11.6 (a), (b) and (c).
Fermi level lies at zero and is shown by black dotted line in Figure 11.6 (a), (b) and (c). Direct band gap of 2.08 eV was observed by applying Hubbard potential of 0.6 eV, which is in good agreement with experimentally observed band gap of hematite (Chamberlin et al. 2015). For further confirmation of band gap and to know magnetic behavior of hematite, partial and total density of states, after applying Hubbard potential, is plotted as given in Figure 11.7 (a) and (b), respectively.

From Figure 11.7 (a), It is observed that top of the valance band is occupied by 2p states of oxygen, while bottom of the conduction band is mostly occupied by 3d states of iron. Hence,
hematite is a charge transfer insulator (Chamberlin et al. 2015) in which the charge from 2p state of oxygen to 3d state of iron is transferred. Due to this transfer, ferromagnetic behavior is observed for GGA+U calculations. This shows that instead of Mott-Hubbard insulator, hematite behaves like charge transfer insulator (Chamberlin et al. 2015). Band gap of 2.08 eV is also confirmed from Figure 11.7 (b). On the basis of these improved optical properties it can be widely used in photovoltaic, photoelectrochemical (PEC) and photovoltaic applications (Chamberlin et al. 2015).

11.4 Summary

Amsterdam density functional software with BAND program was used to investigate electronic properties of hematite at 0K. Optimized basis set of TZ2P and exchange correlation potential of PBE was used in GGA to get converged geometry optimization. Small frozen core was chose with stable cubic crystal structure. Band structure for spin-up and spin-down states for GGA and GGA+U was calculated resulting in 0 and 2.08 eV bang gap energy with reference to the Fermi energy which lies at 0 eV for all cases. Partial and total density of states for hematite without and with Hubbard potential was also plotted and band gap of 0 and 2.08 eV was also observed without and with Hubbard potential of 0.6 eV. Ferromagnetic behavior after applying Hubbard potential was also observed due to charge transfer. These improved electronic properties of hematite with such low value of Hubbard potential are first time reported and makes it a suitable candidate for use in various optoelectronic applications.
Chapter – 12  

Theoretical Investigations – γFe₂O₃

12.1 Introduction

Among various polymorphs of iron oxide, Maghemite (γ-Fe₂O₃) is the second most stable polymorph (Grau-Crespo et al. 2010) having potential applications in various fields such as in biomedical (Nan et al. 2014), optoelectronics (Fouineau et al. 2013) and in gas sensors (Capone et al. 2014). Due to its low cost, chemical stability, biocompatibility and non-toxicity maghemite is widely used in biomedical applications along with other nanoparticles since last 20 years (Fouineau et al. 2013; Grau-Crespo et al. 2010). Structure of maghemite originates from that of spinel magnetite (Riaz et al. 2012). As magnetite structure is made up of a face centered cubic oxygen lattice, divalent cations of iron are occupied at octahedral sites and trivalent cations are distributed at tetrahedral. Distribution of divalent and trivalent cations along with fcc oxygen lattice can be represented as: (Fe³⁺)₆[Fe²⁺Fe³⁺]₁₂O₄. While in case of maghemite, spinel structure is observed due to fcc oxygen lattice in which iron cation vacancies are present on octahedral sites (Fouineau et al. 2013).

12.2 Computational Details for the Investigations of Properties of Maghemite by ADF

Density functional theory was used to theoretically investigate structural and optical properties of maghemite. Amsterdam density functional (ADF) program was used for density functional theory calculations. Generalized Gradient Approximation (GGA) was used for structural optimization of maghemite. The value of Hubbard potential U was set to 0.6 eV for maghemite in GGA+U method. TZ2P was used as basis set, which is of triple-zeta quality and was improved with two sets of polarization functions: 2p and 3d on iron, 2s and 3p on oxygen. Crystal structure was constructed by using atomic positional parameters for maghemite as given in Table 12.1 (Pecharromán et al. 1995).

TABLE 12.1: Atomic positional parameters for Maghemite

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (Tetrahedral)</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.1250</td>
</tr>
<tr>
<td>Fe (octahedral)</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
</tbody>
</table>
We have used frozen-core Perdew-Burke-Ernzerhof (PBE) potentials. 8.33Å Lattice parameter was used after optimization by calculating formation energy for each value of varied lattice parameter. Unit cell volume versus formation energy is given in Figure 12.1.

It is observed from Figure 12.1, that a=8.34 Å gives the converged geometry of maghemite with lowest formation energy (-27 eV) for unit cell volume of 578 Å³. This lattice parameter also shows correlation with experimentally synthesized maghemite given in section 6.4 according to JCPDS card no. 39-1346. Bond angels after geometry optimization were also remains same as for maghemite with cubic unit cell i.e. α=β=γ=90.

Smallest interatomic distance of 4.72 Å was observed after geometry optimization at 0K. This optimized lattice parameter is in good agreement with the experimentally observed lattice constant for maghemite (Disch et al. 2014).

![Figure 12.1: Formation energy versus unit cell volume curve for maghemite.](image)

### 12.3 Results and Discussion

#### 12.3.1 Structural Properties

After getting the geometry convergence, inverse cubic spinel structure for maghemite was observed as given in Figure 12.2. In maghemite, the electronic configuration of Fe²⁺ is 1s² 2s²2p⁶3s²3p⁶3d⁶ and for Fe³⁺ is 1s²2s²2p⁶3s²3p⁶3d⁵. According to this electronic configuration,
Fe\textsuperscript{2+} and Fe\textsuperscript{3+} have six and five unpaired electrons, respectively. In case of maghemite 3d electrons of iron determines structural, electronic and magnetic properties (Sheng-Nan et al. 2014).

Red spheres in Figure 12.2 represent oxygen atoms while yellow spheres represent iron atoms. In this disordered cubic spinel structure, all 32 sites of fcc cubic lattice are fully occupied by oxygen. While 8 tetrahedral sites are occupied by trivalent cations of iron (Fe\textsuperscript{3+}) and 16 octahedral sites are also additionally occupied by of one third of the 13 Fe\textsuperscript{3+} cations (Abe and Watanabe 2014). This structure of maghemite is more complicated due to absence of divalent cations and partial occupation of Fe\textsuperscript{3+} cations on octahedral sites.

Figure 12.2: Structure of super cell of maghemite.

12.3.2 Band Structure and Density of States (DOS)

Band structure is given in Figure 12.3 (a), (b) and (c) to find the band gap at 0K. Fermi level lies at 0 eV and is represented by dotted line in band structure of spin-up and spin down states.
Figure 12.3: a) Band structure of maghemite b) band structure for spin-up states and c) band structure for spin-down states, calculated by GGA.

Figure 12.4 (a) shows partial density of states of s, p and d orbitals of iron cations and s and p orbitals of oxygen anions while Figure 12.4 (b) shows total density of states for spin-up and spin-down states. Fermi level in both cases lies at zero.
Figure 12.4: a) Partial (all states of oxygen and iron) DOS; b) Total DOS of maghemite by using GGA.

From band structure and density of states calculations it was observed that metallic nature for maghemite was observed by using generalized gradient approximation. This underestimation of band gap is due to the self-interaction error (Łazarski et al. 2015). Hubbard potential was applied to GGA to get improved band gap (Schemme et al. 2014).

12.3.3 Band Structure and Density of States with Hubbard Potential (U eV)

After applying Hubbard potential of 0.6 eV on 3d states of iron band structure was plotted as given in Figure 12.5 (a), (b) and (c). Black dotted line at 0 eV shows fermi level. Band gap of 1.97 eV was observed for maghemite by using GGA+U calculations.
Figure 12.5: a) Band structure of maghemite b) band structure for spin-up states and c) band structure for spin-down states, calculated by GGA+U.

Figure 12.6 (a) shows partial density of states for both iron and oxygen and Figure 12.6 (b) shows the total density of states for maghemite with Hubbard potential. From Figure 12.6 (a) it is clear that top of the valence band (near the Fermi level i.e. at 0 eV) is mainly of 2p states of oxygen while in the valance band the occupied 3d levels of iron lie around 15 to 20 eV. On the other hand the bottom of the conduction band (near the Fermi level) is largely populated by the unoccupied p states of iron, and unoccupied 3d levels of iron are present on top of the conduction band with unequal density of states for spin-up and spin-down states.

These results indicate that improved description of the band of maghemite can be obtained by using Hubbard potential as band gap value was improved and came close to experimentally observed values (Mirza et al. 2015). Ferrimagnetic behavior was also confirmed as from Figure 12.6 (b). All these results in a charge transfer from oxygen to iron (anion to cations) and making maghemite a charge transfer insulator (Guo et al. 2010). This nature of maghemite is also confirmed by Hirshfeld charge analysis. For two atoms of iron (Fe1 and Fe2) amount of Hirshfeld charge is observed to be 18.02C, 28.39C, respectively, instead of 26.00C. While for all three oxygen atoms its value increases from 8.00 C to 9.85 C.
This indicates that it is a charge transfer type insulator and due to this property it can be used in spintronics such as in spin-filter devices (Caffrey et al. 2013). From band structure [Figure 12.5 (a)] and DOS [Figure 12.6 (b)] it is clearly observed that the calculated band gap (1.97 eV) for maghemite is well in agreement with experimentally observed one i.e. 2 eV (Mirza et al. 2015). From Figure 12.6 (b) it is observed that DOS is non symmetric near Fermi level. The resulted band gap between minority spin (spin-down) is 2.6 eV while for majority spin (spin-up) it is 1.90 eV. Bottom of the conduction band is higher in energies for spin-down electrons while top of the valance band is rich in energy for spin-down electrons. This change in band gap of energy for majority and minority spins makes maghemite an important candidate for use in spin filter devices as magnetic tunneling barrier. As in these devices, insulator layer is used to control spin of the electrons by using exchange splitting in conduction band. This splitting results in the tunneling of one spin component (Łazarski et al. 2015).

12.4 Summary

BAND code was used to investigate electronic properties of maghemite by using DFT. GGA was used with TZ2P basis set to get all calculations. 8.34Å lattice parameter was used after optimizing by calculating formation energy. Charge transfer for iron and oxygen atoms was observed by Hirshfeld charge analysis. Band structure for minority and majority states were plotted and no band gap was observed at 0K. This underestimation of band gap was removed by applying Hubbard potential. 0.6 eV of lower value of Hubbard potential resulted in improved band gap of 1.97 eV from 0 eV which is in complete correlation with the value obtained experimentally. Partial and total DOS for both calculations (GGA and GGA+U) was plotted and
showed ferrimagnetic behavior of maghemite. Hence, Amsterdam Density Functional (ADF) program can be used to get improved electronic properties with relatively lower value of Hubbard potential, which gives reproducible results in low computer cost.
CHAPTER-13
Chapter – 13  Theoretical Investigations – Fe₃O₄

13.1 Introduction

Magnetite is the commonly observed natural magnet (Rana and Johri 2014). On the basis of its half metallic ferrimagnetic behavior up to its Currie temperature (856K) it has potential applications in many spintronic applications (Parkinson et al. 2012; Carballal et al. 2015). This ferrimagnetic behavior is due to anti-parallel alignment of the octahedral and tetrahedral spins. This alignment is due to spin splitting in the valance region of the 3d electrons of magnetite (Noh et al. 2014). Semiconducting nature in magnetite is also important characteristic of magnetite obtained due to this splitting (Roldan et al. 2013).

Under ambient conditions it is present in inverse cubic spinel crystal structure with general formula of AB₂O₄ where A is bivalent cation and B is usually a trivalent one (Lemine et al. 2012). It can be described by simple face centered cubic lattice of oxygen atoms. Iron (III) cations occupy Fe (A) site i.e. tetrahedral site while Fe (B) site i.e. octahedral site is occupied by mixture of Fe (II) and Fe (III) cations in a ratio of 1:1 (Ramimoghadam et al. 2014). While, at -148 °C (125K) Verwey transition is observed which results in a transition from cubic to monoclinic structure (Yan and Nørskov 2013).

With prompt increase in the memory and processing speed of the computers, nature of matter on atomic and subatomic scale can be investigated by using computer simulations with numerous theoretical techniques. These techniques are quickly becoming a quantitatively accurate and effective method in order to predict structure and various properties of the materials successfully (Dzade et al. 2014). Hence, in order to get improved experimental results, it is important to theoretically investigate various properties of the materials. Herein, among various methods, Density Functional Theory (DFT) is the basic method to theoretically investigate electronic, magnetic and optical properties of iron oxide nanostructures like nanoparticles and thin films (Eom et al. 2014). In this chapter, the results obtained for magnetite by using density functional theory are given.

13.2 Computational Details for the Investigations of Properties of Magnetite by ADF

We have used BAND code in Amsterdam density functional simulation software to perform spin-polarized calculations inside the standard Kohn-Sham application of density functional theory.
Perdew-Burke-Ernzerhof (PBE) functional was implemented as exchange correlation functional in generalized gradient approximation (GGA). Atomic positional parameters used for the construction of the unit cell of magnetite for geometric optimization as given in Table 13.1 (Wechsler et al. 1984).

**TABLE 13.1: Atomic positional parameters for Magnetite**

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 1</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.1250</td>
</tr>
<tr>
<td>Fe 2</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>O</td>
<td>0.2549</td>
<td>0.2549</td>
<td>0.2549</td>
</tr>
</tbody>
</table>

Formation energy was calculated to find the stable crystal structure. Unit cell volume with variation of lattice parameter was calculated and formation energy verses unit cell volume was plotted and given in Figure 13.1. After optimization, lattice parameter $a=8.39 \, \text{Å}$ was used to construct unit cell with internal coordinates: Fe$^{2+}$ (0.1250; 0.1250; 0.1250), Fe$^{3+}$ (0.5; 0.5; 0.5) and O$^{2-}$ (0.2549; 0.2549; 0.2549) (Wechsler et al. 1984). TZ2P basis set was used for both GGA and GGA+U calculations with small frozen core unrestricted calculations. Partial and total Density of states (DOS) was calculated.

![Formation Energy vs Unit Cell Volume](image)

-384
-386
-388
-390
-392
-394
580
585
590
595
600
605
Unit cell volume ($\text{Å}^3$)
Formation Energy (eV)
From Figure 13.2 it is observed that structure with unit cell volume of 593 Å³ possesses the lowest formation energy of -393 eV, which results in the stable and converged structure for further calculations of band structure and density of states. The minimum distance between iron and surrounding oxygen is 3.57 Å, which is in correlation to the experimentally reported value (Yan and Nørskov 2013). Bond angles after geometry optimization remained the same as for magnetite $\alpha=\beta=\gamma=90$.

### 13.3 Results and Discussion

#### 13.3.1 Structural Properties

Figure 13.2 (a) and (b) shows the crystal structure for super cell and unit cell of magnetite. All calculations were carried out on cubic spinel structure with conventional unit cell of 56 atoms with 32 oxygen atoms and 24 iron atoms. Inverse cubic crystal structure was confirmed with space group of Fd3m (227) after geometry optimization.

Figure 13.2 a) crystal structure of super cell of magnetite; b) unit cell. Color scheme Blue= oxygen, yellow= iron.

#### 13.3.2 Band Structure and Density of States (DOS)

Figure 13.3 (a), (b) and (c) shows the band structure of spin-up and spin-down states of magnetite obtained by using GGA at 0K. Fermi level for both states lies at 0 eV showed by dotted lines. For
spin-up and spin-down states Fermi level lies in the conduction band, which results its metallic nature with 0 eV band gap.

![Band structure of magnetite](image1)

**Figure 13.3:** a) Band structure of magnetite b) band structure for spin-up states and c) band structure for spin-down states, calculated by GGA.

Partial density of states for both iron and oxygen is plotted as given in Figure 13.4 (a) and total density of states for magnetite is plotted in Figure 13.4 (b).
Both Figures 13.4 (a) and (b) confirm the band gap of 0eV for these sets of calculations. Bottom of the valance band is mainly dominated by 2p state of oxygen but the contribution of the 3d band of iron near the Fermi level is not dominated as seen from Figure 13.4 (a).

**13.3.3 Band Structure and Density of States with Hubbard Potential**

Band structure and density of states of magnetite by applying Hubbard potential are given in Figures 13.5 (a-c) and 13.6 (a-b), respectively. Improved band structure and DOS was obtained by using U=0.6 eV.
From Figure 13.5 (a) band gap of 0.89 eV is observed which is also confirmed from total density of states of magnetite [Figure 13.6 (b)] obtained after applying Hubbard potential of 0.6 eV. Charge transfer from 2p states of oxygen to 3d states of iron is observed from Figure 13.6 (a).

From Figure 13.6 (b) it is observed that a small band gap of 0.89 eV is observed for low symmetry magnetite. While half metallic nature with ferromagnetic behavior of magnetite [Figure 13.5 (b)] is due to the presence of continuous bands of minority spins near the Fermi level. Hence, on the basis of these electronic and optical properties magnetite can be used in various spintronic devices (Bosak et al. 2013).

13.4 Summary
In conclusion, ADF program was used to investigate structural, electronic, optical and magnetic nature of magnetite by applying density functional theory at 0K. Lattice parameter of 8.39 Å was used with bond length between iron and oxygen to construct unit cell. Lowest formation energy of -393 eV was obtained for magnetite with unit cell volume of 593 Å³. Geometry optimization was achieved for this stabilized cubic spinel structure by using small frozen core PBE exchange correlation potential with TZ2P basis set. Hubbard potential of U=0.6 eV was applied for iron to get improved band gap of magnetite. Band structure for states with spin up and down of both oxygen and iron were plotted for both calculations and gave 0eV for GGA and 0.89 eV for GGA+U. Partial and total density of states also confirmed the observed band gap in both cases also half metallic ferromagnetic behavior of final magnetite was also confirmed by GGA+U calculations. These low value of Hubbard potential applied in Amsterdam density functional can yield reproducible and improved results on low cost of computer power and time.
CHAPTER-14
Chapter – 14  Theoretical Investigations – FeO added ZnO

14.1 Introduction

Nanostructures of semiconducting materials with wide band gap and improved magnetic properties are currently attracting lot of attention of researchers due to their important role for the development of nanoscale technologies. Among various research-oriented nanostructures of semiconducting materials, iron oxide doped ZnO nanostructures are theoretically investigated here to study the correlation between experimentally obtained properties and with theoretically obtained ones. Some of the properties investigated by using Amsterdam density functional package are given here.

14.2 Computational Details

Structural, electronic, optical and magnetic properties of iron oxide doped ZnO nanostructures were investigated by using Amsterdam density functional (ADF) package. In the first step geometry optimization was carried out using BAND code by first selecting space group of ZnO (as in this case of iron oxide doped nanostructures host material is ZnO); P63mc (186) was used. Lattice parameters were selected after optimization and geometry convergence was achieved for \(a=b=3.247\ \text{Å}\) and \(c=5.2046\). Crystal structure of iron doped ZnO was modeled using hexagonal unit cell comprising of six formula units. Basis set, TZ2P was employed in a periodic system for the solution of Kohn-Sham equations involved in density functional theory. Un-restricted calculations were performed with widely used generalized gradient approximation (GGA). Perdew-Burke-Ernzerhof (PBE) was the form of functional used in the approximation. GGA+U approach with \(U=0.6, 0.7\) and \(0.8\) eV for iron, Mn and Zn, respectively was applied in order to correct electronic correlation of 3d electrons of iron and Zn. To the best of our knowledge it is the smallest value of \(U\) ever reported. 2x2x2 Supercell was used to sample Brillouin zone and Band structure of iron doped ZnO.

14.3 Results and Discussion

Figure 14.1 (a) and (b) shows 2x2x2 super cell of ZnO (having 16 No. of atoms) with Fe doping and with Mn/Fe co-doped ZnO, respectively. Hexagonal wurtzite structure was observed for both cases after geometry optimization. Bond angles also remained same as \(\alpha=\beta= 90\), \(\gamma=120\).
These parameters were then further used for other calculations such as for band structure and density of states calculations.

The calculated band structure is plotted in Figure 14.2. Hubbard potential of 0.6 and 0.8 eV for Fe and Zn was used, respectively. Band structure for majority spin and minority spin states is shown by red color and blue color respectively. While in case of Mn/Fe co-doped ZnO band structure was calculated by using 0.6, 0.8 and 0.7 eV Hubbard potential for Fe, Zn and Mn respectively and is given in Figure 14.3.

Fermi level (shown by black line) lies at zero for both spin-up and spin down states. Direct band gap of 3.41 eV was observed, which is in good agreement with experimentally observed band gap of Fe doped ZnO nanostructures with 4wt % concentration of Fe. While improved band gap of 3.48 eV was obtained for Mn/Fe co-doped ZnO.

Figure 14.1: a) Supercell of iron doped ZnO and b) supercell of Mn/Fe co-doped ZnO (Golden atoms=Fe, Silver=Zn, Red=O and Green=Mn).

Figure 14.2: Band structure of Fe doped ZnO calculated by GGA+U.
Figure 14.3: Band structure of Mn/Fe co-doped ZnO calculated by GGA+U.

Partial and total density of states for Fe doped ZnO is given in Figure 14.4 and is also in accordance with the band structure of Fe doped ZnO calculated by GGA+U.

Figure 14.4: Density of states of Fe doped ZnO calculated by GGA+U.

Figure 14.5: Density of states of Mn/Fe co-doped ZnO calculated by GGA+U.
These theoretical results are in close correlation with the experimentally obtained results with improved optical and magnetic properties. Figure 14.5 shows density of states for Mn/Fe co-doped ZnO.

14.4 Summary

Amsterdam density functional software with BAND program was used to investigate electronic properties of iron oxide doped ZnO nanostructures. Optimized basis set of TZ2P and exchange correlation potential of PBE was used in GGA to get converged geometry optimization. Small frozen core was chosen with stable hexagonal wurtzite crystal structure. Band structure for spin-up and spin-down states for GGA and GGA+U was calculated that resulted in 3.41 and 3.48 eV bang gap energy with reference to the Fermi energy which lies at 0 eV for Fe doped and Mn/Fe co-doped ZnO, respectively.
Conclusions

In conclusion nanostructures such as nanospheres, nanorods, nanobrushes, nanoneedles, and cubic nanospheres of magnetite, maghemite and hematite phases of iron oxide along with iron and Mn/Fe codoped ZnO have been fabricated. All these nanostructures were experimentally synthesized by using application oriented and economical sol-gel method. The main issues addressed in this research work were synthesis of different iron oxide based nanostructures and the correlation of obtained structural, magnetic and optical results with theory.

Iron chloride and zinc acetate were used as precursors for synthesis of different iron oxide based nanostructures. Molarity of the sols, pH and temperature are the important parameters to control morphology of iron oxide based nanostructures. Various surfactants were also tested for optimization of these nanostructures. BAND module in Density Functional Theory (DFT) based Amsterdam Density Functional (ADF) software was used for theoretical investigations of these iron oxide nanostructures. The correlation of experimentally observed results with the theoretically obtained results showed that structural confirmation was done with calculated lattice parameters for all nanostructures.

Summary of each part is given as under:

1. Firstly, with the variation of molarity of sols from 1.8 to 0.6 mM, different iron oxide nanostructures were observed.
   a. For 1.8mM mixed phases of magnetite and maghemite were observed with morphology of nanorods having 70nm diameter and 165nm length.
   b. For 1.6mM mixed phases of magnetite and maghemite were observed with morphology of mixed nanorods and nanospheres.
   c. For 1.4mM pure magnetite phase was achieved with morphology of nanospheres having 110nm diameter and higher saturation magnetization.
   d. For 1.2 and 1.0mM mixed phases of magnetite and maghemite were observed with morphology of nanospheres having 200nm diameter.
   e. For 0.8. mM mixed phases of magnetite and maghemite were observed with morphology of nanospheres but with some agglomeration.
   f. For 0.6mM mixed phases of magnetite and maghemite were observed with morphology of nanoneedles/brushes having different diameters and lengths.

2. In second part optimized molarity of 1.4mM was used and pH of the sols was varied between 1-9.
a. With pH 1 and 2 magnetite phase was obtained having morphology of nanospheres with 50nm diameter and superparamagnetic behavior with high saturation magnetization of 70emu/g. The band gap for magnetite nanoparticles was 2.81eV for pH 1.

b. For pH 3, hematite phase was observed with nanospherical morphology having 50-100nm diameter and saturation magnetization of 47emu/g. These nanoparticles were reported to have band gap of 2.08eV.

c. With further increase in pH from 5-9 magnetite phase was achieved. Spherical morphology with 100nm diameter for hematite nanoparticles was observed. The maximum value of band gap in case of maghemite nanoparticles was 1.97eV.

d. Effect of calcination confirmed the strengthening of the obtained phases only. No conversion of one phase to the other was observed by increasing calcination temperature in our case. Increased crystallinity and saturation magnetization was observed at calcination of 300°C.

e. Hence by controlling molarity and pH magnetite, maghemite and hematite nanostructures were obtained with different morphologies such as nanospheres, nanorods, and nanobrushes.

3. After optimization of molarity, pH and temperature, in the third step superparamagnetic Fe₃O₄ nanoparticles were synthesized because of their wide usage in biomedical applications.

Synthesis of magnetite nanoparticles with controlled size i.e. ≥50nm was a major task in current research as agglomeration of nanoparticles affected this. Various surfactants, such as PVA, triton X-100 and oleic acid were tested. In order to avoid agglomeration of magnetite nanoparticles use of oleic acid as surfactant was successful. Stability of these nanoparticles for biomedical use is also important and therefore these two parameters were optimized in this part of the research work. The amount of oleic acid was varied as 5%, 10% and 15% by volume. Calcination temperature was varied in the range of 300°C-900°C.

a. Iron oxide sol with 15% by volume of oleic acid at 500°C showed superparamagnetic behavior with morphology of cubic spheres having 25nm diameter. These cubic nanoparticles also have highest dielectric constant of ~107.5 (log f = 5.0) prepared under same conditions.

b. Dia-ferromagnetic and para-ferromagnetic mixed behavior of sols was observed for samples with 5% and 10% oleic acid by volume. Low oleic acid content resulted in formation of mixed iron oxide phases.
c. Two types of NPs were observed in SEM images one with shell and one without shell with 10% oleic acid.

4. Due to requirements of wide band gap materials with high saturation magnetization, in the next part of research work ZnO was used as host material and doping of iron was done to get new improved material with better magnetic properties and high value of band gap. The dopant concentration was varied as 1wt% to 5wt%. Zinc acetate and iron chloride were used as precursors and iron was reduced by using reducing agent from Fe₂O₃ sol.
   a. With addition of dopant in ZnO lattice the peak positions shifted to higher angles indicating that the dopant was successfully incorporated in the host lattice till 4% doping.
   b. Iron doped ZnO nanoparticles showed high saturation magnetization of 0.91emu/g with 5wt% doping.
   c. Increased value of transmission i.e. more than 80 % in the visible region was achieved in as-synthesized nanoparticles.
   d. The increase in the band gap value from 3.05eV to 3.48eV was observed with increase in iron concentration.

5. Co-doping of Mn/Fe was done to investigate structural, optical, and magnetic properties of Mn/Fe co-doped ZnO nanoparticles. Five different sols were synthesized with 1-5wt% concentration along Mn and Fe ratio of 1:1. Glass and copper substrates were used to deposit Mn/Fe co-doped ZnO nanostructures in the form of thin films. Annealing of the deposited thin films in the presence of magnetic field at 300 °C for 1 h was done.
   a. XRD results showed incorporation of Mn and Fe in the host lattice up to a dopant concentration of 4wt%. However, small crystallites of Mn and Fe₂O₃ are observed by increasing the dopant concentration to 5wt%.
   b. VSM results indicated room temperature ferromagnetism in all samples. Low value of shape anisotropy was observed in the case of Mn doped ZnO. However, no shape anisotropy was observed in the case of co-doped thin films. Moreover, Mn/Fe co-doped thin films showed magnetic hysteresis equivalent to that of multilayered structure, indicating that such complex structures can be used in spintronic devices can replacing multilayers by a single ZnO layer with co-doping of Mn and Fe.

6. Wüstite is one of the important phases of iron oxide having simple cubic structure. We first optimized various parameters for iron by using this crystal structure. In case of wüstite optimization of Approximations, Hubbard potential and exchange correlational potential showed that:
a. Optimized formation energy resulted in 4.33 Å value of lattice parameter, which is in close agreement to its experimental value.

b. Results obtained by GGA were in good correlation to the experimental results as compared to those of LDA. So, GGA was used for all calculations of hematite, magnetite and maghemite.

c. Hubbard potential was optimized by varying it in the range 0.1-1 eV, and 0.6 eV was the value at which results were found to be in correlation with the experimental results. So for all calculations 0.6 eV value was applied.

d. Different exchange correlational potentials using GGA were also optimized. This optimization of different parameters strongly based on the condition that the optimized parameter must give particular results in accordance to experimental results, so that these nanostructures can be utilized in various applications. Hence, in case of exchange correlational potential PBE was used.

7. Structural analysis proved the formation of hematite nanostructures with accurate correlation to the experimental values.

a. GGA calculations for 30 atoms of hematite confirmed its n-type semiconducting nature with 0 eV value of band gap and antiferromagnetic nature, which was confirmed by DOS.

b. 2.08 eV band gap with GGA+U confirmed correlation of theory to the experimentally observed band gap for nanoparticles synthesized with 1.4 mM molarity at pH 3. Magnetic properties were also in accordance with the experiment results. Analysis of the density of states confirmed strong hybridization between Fe 3d and O 2p states in iron oxide.

8. Electronic properties calculated with 56 no of atoms for magnetite proved that it has band gap of 2.81 eV is in correlation with the band gap reported for experimentally synthesized magnetite at 1.4 mM sol concentration and pH 1. Semi-metallic behavior of magnetite was also confirmed in case of theoretical investigations by GGA+U.

9. Electronic properties calculated with 48 no of atoms for maghemite proved that it has band gap of 1.97 eV was in correlation with the experimentally reported band gap of magnetite formed at 1.4 mM sol concentration at pH 9.

10. In all cases (magnetite, maghemite and hematite) density of states plots confirmed that the main reason for the magnetic properties in iron oxide based nanostructures was the d orbital electrons.
REFERENCES


strategy for targeting the central nervous system using magnetic albumin nanospheres.

*Journal of Biomedical Nanotechnology, 8*(1), 182-189.


Wanaguru, P., An, J. and Zhang, Q. (2016). DFT+U study of ultrathin α-Fe2O3 nanoribbons from (110) and (104) surfaces. *Journal of Applied Physics, 119*(8), 084302.


Appendix

List of Publications

   **Authors:** R. Ashraf, U. Khan, M. Bashir, S. Riaz and S. Naseem  
   **I.F.:** 1.422

   **Authors:** S. Riaz, R. Ashraf, A. Akbar and S. Naseem  
   **I.F.:** 1.422

   **Authors:** S. Riaz, R. Ashraf, A. Akbar and S. Naseem  
   **I.F.:** 1.422

   **Authors:** A. Akbar, S. Riaz, R. Ashraf and S. Naseem  
   **I.F.:** 1.422

   **Authors:** S. Riaz, M. Azam, R. Ashraf and S. Naseem  
   **I.F.:** 1.422

   **Authors:** A. Akbar, S. Riaz, R. Ashraf, S. Naseem  
   **I.F.:** 1.66

   **Authors:** R. Ashraf, T. Mahmood, S. Riaz and S. Naseem  
   **I.F.:** 0.514

   **Authors:** R. Ashraf, S. Riaz, Z. N. Kayani and S. Naseem

   **Authors:** R. Ashraf, S. Riaz, Z. N. Kayani and S. Naseem

    **Authors:** R. Ashraf, S. Riaz, S. S. Hussain and S. Naseem
Papers Presented Internationally and Nationally

1. **Structural and Magnetic Properties of Sol-Gel Synthesized Mn/Fe co-doped ZnO Thin Films**, International Symposium on Advanced Magnetic Materials and Applications, ISAMMA 2013, held on 21-25th July 2013, Taichung, Taiwan.
   R. Ashraf, S. Riaz, U. Khan and S. Naseem

   R. Ashraf, S. Riaz, M. Bashir and S. Naseem

   R. Ashraf, S. Riaz and S. Naseem

   S. Riaz, R. Ashraf, R. Noor and S. Naseem

   R. Ashraf, S. Riaz and S. Naseem

   R. Ashraf, S. Riaz and S. Naseem

   R. Ashraf, S. Riaz, M. Akhtar, S. Naseem

8. **Synthesis and Characterization of ZnO Nanoparticles through Sol-Gel Route**, National Meeting on Nanotechnology Research in Pakistan, August 03, 2010, Lahore, Pakistan.
   R. Ashraf, S. Riaz and S. Naseem

   M. Azam, R. Ashraf, M. Sulaiman, S. Riaz and S. Naseem

    R. Ashraf, S. Riaz and S. Naseem
   M. Iqbal, **R. Ashraf**, M. A. Naseer, S. Riaz and S. Naseem

   M. Azam, A. Yar, **R. Ashraf**, S. Riaz and S. Naseem

   **R. Ashraf**, M. Tahir, N. Iqbal, S. Riaz and S. Naseem

   S. Zaman, W. Azeem, **R. Ashraf**, S. Riaz and S. Naseem

   **R. Ashraf**, S. Riaz, Z. N. Kayani and S. Naseem


   **R. Ashraf**, S. Riaz, N. Ali and S. Naseem


   M. Azam, A. Habiba, **R. Ashraf**, S. Riaz and S. Naseem

   **R. Ashraf**, S. Riaz, M. Bashir, U. Khan and S. Naseem

   **R. Ashraf**, T. Mahmood, S. Riaz, S. Naseem
R. Ashraf, S. Riaz, T. Mahmood, S. Naseem

R. Ashraf, T. Mahmood, M. Azam, S. Riaz, S. Naseem

R. Ashraf, S. Riaz, T. Mahmood, S. Naseem

R. Ashraf, M. Azam, T. Mahmood, S. Riaz, S. Naseem

R. Ashraf, T. Mahmood, S. Riaz and S. Naseem
Structural and Magnetic Properties of Mn/Fe Co-Doped ZnO Thin Films Prepared by Sol–Gel Technique

Robina Ashraf, Saira Riaz, Mahwish Bashir, Usman Khan, and Shahzad Naseem

Centre of Excellence in Solid State Physics, University of the Punjab, Lahore 54590, Pakistan

Mn/Fe co-doped ZnO thin films are prepared by simple sol–gel and spin coating method. Five different sols with the change in concentration (1–5 wt%) of both Mn and Fe are synthesized. Molar ratio of Mn and Fe is kept constant, i.e., 1:1. Sols are spun onto glass and copper substrates by spin coating method followed by the post magnetic field annealing at 300 °C for 1 h. Effect of Mn and Fe codoping on ferromagnetic properties of ZnO is reported in this paper. Structural and magnetic properties of as prepared and annealed samples are investigated by X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM). Scanning electron microscope is used to study the surface morphology of co-doped films. XRD results show incorporation of Mn and Fe in the host lattice up to a dopant concentration of 4 wt%. However, small crystallites of Mn and Fe2O3 are observed by increasing the dopant concentration to 5 wt%. VSM results indicate room temperature ferromagnetism in all samples without the presence of any secondary phases. Low value of shape anisotropy is observed in the case of Mn doped ZnO. However, no shape anisotropy is observed in the case of co-doped thin films. Moreover, Mn/Fe co-doped thin films show magnetic hysteresis equivalent to that of multilayered structure, indicating that such complex structures used in spintronic devices can be replaced by a single ZnO layer with codoping of Mn and Fe.

Index Terms—Diluted magnetic semiconductors (DMSs), Fe/Mn co-doped ZnO, ferromagnetism, sol–gel.

I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have gained much interest in the field of optoelectronic devices and spintronics due to the involvement of both charge and spin of electrons [1]–[3]. Zinc oxide is one of the promising materials to obtain DMSs due to its wide bandgap at room temperature, i.e., 3.37 eV and large exciton binding energy, i.e., 60 meV. Doping of much smaller amount of transition metals (Mn, Fe, Co, Ni, In, V, and Cr) [4]–[10] plays an important role in the structural and magnetic properties of zinc oxide to act as DMSs. Compatibility of Mn in ZnO is because of its close resemblance of ionic radii with Zn along with its thermal solubility. Mn has effective electron mass ∼0.3 me (me is free electron mass) that results in large injected spins and charge carriers making Mn:ZnO useful for the spintronic nanodevices [11]. Fe is also one of the important candidates for doping to obtain the DMSs. Goktas et al. [14] reported the influence of Fe doping on ZnO thin films deposited by sol–gel spin coating method to observe the room temperature magnetism.

Codoping of various transition metals plays an important role in the improvement of structural, optical, and magnetic properties of DMSs. Chakrabarti et al. [13] reported room temperature ferromagnetism in Mn/Fe co-doped ZnO by solid-state reaction method and found that the codoping of Mn/Fe improves magnetic properties as compared to un-doped materials. Xu et al. [14] reported the synthesis of Cu and Co co-doped ZnO using sol–gel method to investigate the effect of shape and hydrogenation on the magnetic properties of synthesized nanopowder.

Room temperature ferromagnetism in the transition metal co-doped zinc oxide nanostructures is also the topic of interest for researchers during the last few years. The origin of magnetism in DMSs is different according to different groups of researchers. Hailing et al. [15] reported that room temperature ferromagnetism in (Fe, Mn) co-doped ZnO thin films is sensitive to oxygen and Zn vacancies, while Fan et al. [1] reported that the presence of room temperature ferromagnetism is due to clusters of the doping transition elements. Previously, our group has reported room temperature ferromagnetism in un-doped ZnO thin films because of the presence of Zn vacancies [16].

Un-doped and doped ZnO thin films have been prepared by different techniques, such as pulsed laser technique [1], chemical vapor deposition [17], coprecipitation method [18], RF magnetic sputtering [19], and sol–gel method [16], [20].

In this paper, we report the synthesis of Mn/Fe co-doped ZnO sol using sol–gel method. Thin films were achieved by spin coating onto suitable substrates (glass and copper) to achieve multilayered effect. To the best of our knowledge, there are no reports on Mn/Fe co-doped ZnO thin films by sol–gel method to date. Effect of codoping of Mn and Fe on structural and magnetic properties of ZnO is studied.

II. EXPERIMENTAL DETAILS

Sol–gel method is used for the synthesis of un-doped and Mn/Fe co-doped ZnO sols. Zinc acetate bi-hydrate [Zn(CH₃COO)₂·2H₂O], iron nitrate nona-hydrate [Fe(NO₃)₃·9H₂O] and manganese (II) acetate tetra-hydrate [C₂H₆MnO₄·4H₂O] were used as precursors, whereas IPA, TEA, and ethylene glycol were used as solvents. In the first step, ZnO sol was synthesized; detailed description for the synthesis of ZnO sol has been reported earlier [16]. In the second step, Mn doped ZnO sols were synthesized [21]. In the third step, for the Mn/Fe co-doped ZnO thin films, three solutions were prepared to get the final Mn/Fe co-doped ZnO sols. The dopant concentration was varied in the range of 1–5 wt%. The 1:1 molar ratio of Mn and Fe was used. MnFeO sol was synthesized by dissolving 0.245 g of C₄H₆MnO₄·4H₂O and [Fe(NO₃)₃·9H₂O] in ethylene glycol.
glycol under constant magnetic stirring for 1 h. Mn/Fe co-doped ZnO sol was obtained by drop wise addition of dopant sol in the freshly prepared ZnO sol. Co-doped sols were stirred continuously at room temperature for 4 h. Transparent sols were obtained for doping concentration up to 4 wt%. However, the colorless transparent sol changed to grayish black transparent color with the increase in doping concentration to 5 wt%. Mn/Fe co-doped ZnO sols were spin coated on a cleaned glass and copper substrates at 3000 r/min for 30 s, followed by magnetic-field annealing at 300 °C for 1 h. Crystalline structure and phase of the films was observed using Rigaku D/Max II-A X-ray diffractometer (XRD) with CuKα (λ = 1.5405 Å). The diffraction angle was adjusted from 20° to 80° with step width of 0.02°. Lakeshore 7407 vibrating sample magnetometer was used to study hysteresis loop of the samples. Hitachi S-3400N scanning electron microscope (SEM) was used to investigate the surface morphology of doped films.

III. RESULTS AND DISCUSSION

A. Structural Characterization

Fig. 1 shows XRD pattern of 5 wt% Mn-doped ZnO thin film, which has been reproduced from our previous paper [21]. It was observed that up to 5 wt% doping of Mn, there are no structural changes in ZnO wurtizite structure and no peak corresponding to Mn2O3 was observed. The absence of dopant oxide and metal diffraction peaks in Fig. 1 indicate that Mn has successfully replaced Zn in the host lattice, hence forming DMS [22]. Wurtzite structure is noncentrosymmetric and hence more favorable for inducing and studying magnetism in this material [16]. Mn concentration incorporated into ZnO lattice was estimated to be ∼2.6% by following Vegard’s law for 5 wt% doped ZnO thin film. Solid solubility limit of Mn in ZnO matrix is about 13% [23]. That is why Mn concentration of the 5 wt% (nominal composition) is too low to change the wurtzite structure of ZnO.

XRD patterns of un-doped and Mn/Fe co-doped ZnO are shown in Fig. 2. Presence of high intensity peaks (100), (002), and (101) gives clear evidence of the formation of hexagonal wurtzite structure of ZnO. XRD results show that codoping up to 4 wt% [Fig. 2(b)] did not change the hexagonal wurtzite crystal structure. However, as the dopant concentration was increased to 5 wt%, small diffraction peaks corresponding to Mn/Fe2O3 (JCPDS card nos. 32-0637 and 39-1346 respectively) are observed as shown in Fig. 2(c).

The average crystallite size (D) calculated from the XRD data using Scherer’s formula is in the range of 12–19 nm with the variation in dopant concentrations.

B. Surface Morphology

Fig. 3 shows SEM images of Mn/Fe co-doped ZnO thin films. It is clearly observed from Fig. 3 that average grain size decreases with increase in concentration of dopant elements up to 4 wt%. Decrease in crystallite size might have been observed because of the smaller ionic radii of manganese and iron as compared with zinc. This can be observed from increment in full-width at half maximum of the XRD peaks as the dopant’s concentration increases. However, increase in crystallite size up to 19 nm was observed with the further increase in dopant concentration to 5 wt%. Slight shifting of peaks for Mn/Fe co-doped sample toward lower angle is due to the stresses present in the film. As the number of dopant atoms increases at the substitution sites, stresses due to difference in ionic radii of dopants and host lattice atoms are produced [7]. The shift in peak positions with increase in Mn/Fe doping concentration indicates the expansion of the lattice parameters [7].

Fig. 3. SEM micrographs of the Mn/Fe co-doped ZnO thin films with (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt%, and (e) 5 wt%.

Fig. 1. XRD pattern of Mn-doped ZnO thin film [21].

Fig. 2. XRD graphs of (a) un-doped, (b) 4 wt% and (c) 5 wt% Mn/Fe co-doped ZnO thin films (*Mn/Fe2O3).
diameter of 80 nm and length of 200 nm. By increasing the dopant concentration to 2 wt%, nanostructure changed from nanorods to nanospheres with a diameter of 150 nm [Fig. 3(b)]. The size of nanostructure further reduced to 100 nm by increasing the dopants to 4 wt%, as shown in Fig. 3(c) and (d). This might be due to the fact that Mn and Fe ions could affect the ZnO crystal lattice at nanoscale and alter the preference of the crystal growth from rod-like to nanospheres. By increasing the dopants concentration to 5 wt%, agglomeration occurred, as shown in Fig. 3(e), due to which the magnetization value also reduced as shown by the vibrating sample magnetometer results in Section III-C.

C. Magnetic Characterization

Fig. 4 shows hysteresis of Mn-doped ZnO with ferromagnetic nature. It was observed that the squareness and magnetization of sample increase with increase in Mn content in the range of 1–5 wt% (M1–M5). High squareness of ferromagnetic behavior can be employed in the switching operation for spintronic devices [3], [17].

Fig. 5 shows multilayered structure like hysteresis of Mn/Fe co-doped ZnO thin films. Wu et al. [25] reported similar results by the deposition of stacked layers of different magnetic oxides. However, such results are observed in the present study by simple codoping of transition metals using sol–gel technique. Saturation magnetization increased with the increase in dopant concentration from 1 to 3 wt%. Saturation magnetization and squareness is plotted as a function of doping concentration in Fig. 6. Coupled magnetic moments of dopant atoms (Mn/Fe) has lowered the formation energy for Zn vacancies and enhanced ferromagnetic behavior [1].

Hole-mediated exchange interactions are also responsible for ferromagnetic behavior due to an introduction of hole by the exchange of Fe$^{3+}$ ions with Zn site in Fe-doped ZnO. Charge transfer in mixed valence electrons was predicted as the origin of ferromagnetism in Co/Fe co-doped ZnO [26]. It can be related to multilayered structure where during charge transfer an additional charge from the dopant results in magneto-electronic coupling, which results in layering structures [7] as was observed in Fig. 5.

In the present study, Mn/Fe co-doped ZnO samples showed much stronger ferromagnetic behavior as compared to that reported in literature [1], where co-doped films were prepared using PLD after mixing and annealing (up to 800 °C for several hours) the powders by solid-state reaction; the comparison is given in Table I. There are many possible origins for the presence of ferromagnetism in the multilayered structures. First reason is the formation of the secondary phases [19], but this option can be easily ruled out as XRD (Fig. 2) shows that there were no peaks of the secondary phase. Second possibility is the presence of diffraction peaks corresponding to metals [19] since Mn and/or Fe both can be the dominant source of the ferromagnetism, but again XRD results clearly show the absence of metal diffraction peaks up to dopant concentration of 4 wt%.

Now, the third reason for ferromagnetic behavior is RKKY interaction between conductive electrons of ZnO and spin-polarized electrons of Mn$^{2+}$ and Fe$^{3+}$ ions in case of Mn/Fe co-doped ZnO thin films. Such interactions can appear because of the spin polarization of conductive electrons in the ZnO host lattice. In addition, after the exchange interaction with local spin polarized electrons of Mn and Fe ions, these local spin polarized electrons exhibit same spin direction as conductive electrons after long range exchange interaction. Thus, due to this exchange interaction material shows ferromagnetic properties [27]. Another strong reason, reported previously [16] in the case of room-temperature ferromagnetism in un-doped ZnO
thin films, is the presence of Zn vacancies. Table I shows the comparison of $M_s$ values of un-doped, Mn-doped and Mn/Fe co-doped ZnO thin films prepared by sol–gel and spin coating method. It can be seen in Table I that Mn and Fe co-doped ZnO thin films show high saturation magnetization as compared with the un-doped and Mn-doped ZnO thin films. It is important to mention here that these magnetic properties are much enhanced as compared to those reported in the literature.

IV. CONCLUSION

Thin films of Mn/Fe co-doped ZnO were successfully prepared by simple and economic sol–gel method and spin coating method. The dopant concentration of Mn/Fe was varied in the range 1–5 wt%, XRD data showed the incorporation of transition metal ions without formation of oxides of dopants up to 4 wt%. SEM results indicated the formation of nanorods at 1 wt% of Mn/Fe codoping in ZnO thin films. Increase in dopant concentration not only affected the shape from rods to spherical but also has varied the grain size. Thin films showed magnetic hysteresis with high saturation magnetization for 3 wt% Mn/Fe co-doping. Shape of $M–H$ curves is similar to that of the multilayered structure indicating that such complex structures can be replaced by a single ZnO layer with codoping of Mn and Fe.

REFERENCES

Study of the structural and electronic properties of FeO at the LDA and GGA level

Robina Ashraf\textsuperscript{a,1,*}, Tariq Mahmood\textsuperscript{b}, Saira Riaz\textsuperscript{a}, Shahzad Naseem\textsuperscript{a}

\textsuperscript{a}Centre of Excellence in Solid State Physics, University of the Punjab, Lahore 54590, Pakistan
\textsuperscript{b}Department of Physics, Government College Women University, Sialkot 51110, Pakistan

A R T I C L E   I N F O
Article history:
Received 27 April 2017
Revised 19 May 2017
Accepted 19 May 2017
Available online 15 June 2017

Keywords:
FeO
Density functional theory
Amsterdam density functional
GGA
LDA
Hubbard potential

A B S T R A C T
Due to its strongly correlated insulating nature, FeO is used in various catalytic applications. Structural and electronic properties of FeO are investigated by using density functional theory (DFT) with the BAND code in Amsterdam Density Functional (ADF) software at ambient conditions. The generalized gradient approximation (GGA) and local density approximation (LDA) without and with the Hubbard potential (U eV) are used to investigate the structural and electronic properties of FeO. Geometric optimization of FeO is carried out by using the LDA and GGA method. CAPZ (Ceperley–Alder–Perdew–Zunger) and PBE (Perdew–Burke–Ernzerhof) are used as exchange correlation potentials for the LDA and GGA, respectively. The Hubbard potential is optimized and U=0.6 eV is used to overcome the under-estimation of the band gap of FeO in both approximations. The band structure shows the metallic nature of FeO with the GGA and LDA while band gap of 2.34 and 2.08 eV is observed by using GGA+U and LDA+U, respectively. Our calculated band gap value with the GGA+U is in good agreement with the reported experimental value, i.e. 2.4 eV. The total and partial density of states are also plotted to show the band structure. To the best of our knowledge, no study has been reported yet at the U=0.6 eV value of the Hubbard potential.

© 2017 The Physical Society of the Republic of China (Taiwan). Published by Elsevier B.V. All rights reserved.

1. Introduction

Different phases of iron oxide play significant role in a range of disciplines like biology, physics, geology, chemistry and medicine, which makes them a research oriented material both experimentally and theoretically [1,2]. Among these phases magnetite, hematite and wüstite are mostly used in heterogeneous catalysts as common compositions [1]. For example, these phases are key components in Fischer–Tropsch synthesis (FTS). Fischer–Tropsch synthesis is an important method for obtaining valuable chemicals (liquid alkanes) for clean liquid fuels (jet fuels and gasoline diesel) using syngas, which refers to a mixture of H\textsubscript{2} and Co [3]. Reduction and carburization are the main behaviors of these iron oxide phases involved in FTS.

Wüstite, one of these important phases of iron oxide, is a strongly correlated insulator with a band gap of $\sim$2.4 eV [4]. This insulating nature of wüstite is due to the charge transfer process from the 2p state of oxygen to the 3d state of iron.

\textsuperscript{*} Corresponding author.
\textsuperscript{1} E-mail address: robina.ashraf206@yahoo.com (R. Ashraf).
\textsuperscript{1} Part of Ph.D. thesis of first author.

http://dx.doi.org/10.1016/j.cjph.2017.05.026
0577-9073/© 2017 The Physical Society of the Republic of China (Taiwan). Published by Elsevier B.V. All rights reserved.
[5]. It exists in a NaCl type cubic crystal structure at ambient conditions [6]. The electronic structure of wustite shows antiferromagnetic behavior below its Néel temperatures i.e. 198 K [7].

Wüstite has challenged experimentalists and theorists for over 60 years due to its structure and properties [7]. Hence it is important to investigate its structural and electronic properties like the electronic band gap using the density functional theory (DFT). A theoretical understanding of FeO has been acquired in the last five decades by using computational approaches based on first principle calculations [8]. The DFT is a widely used method for studying the electronic structure of these transition metal based compounds [9].

The generalized gradient approximation (GGA) and the local density approximation (LDA) are the most commonly used approximations in DFT based investigations [10]. But both the GGA and LDA do not describe the true nature of transition metal based materials. In these materials the 3d orbitals are partially occupied, and this therefore results in a metallic nature of the compound instead of its experimentally reported insulating state [11]. In order to overcome these underestimations, the LDA and GGA were used with the Hubbard potential U to get results that were comparable to the experiments [12]. In the literature, different research groups used different values of the Hubbard potential U in order to calculate the band gap and other properties by using different DFT based softwares [9]. Wdowik et al. [7] reported a 2.2 eV band gap by using the value of the Hubbard potential of 5 eV in the VASP code. Eom et al. [4] selected the value of the Hubbard potential of 4.2 eV to investigate the electronic and optical properties of wüstite. Spiridis et al. [13] used U=3 eV for the investigation of the structural and magnetic properties of the same material.

In this paper, we have investigated the structural and electronic properties of FeO by using the LDA and GGA with and without the Hubbard Potential (U). Regarding the structural properties, we have investigated the bond length, formation energy and lattice parameter. The band structure, partial density of states and total density of states are also reported to describe the electronic properties of FeO.

2. Computational details

Structural and electronic properties of FeO were investigated using the LDA and GGA methods based on the DFT at ambient conditions. The BAND (Band structure Program) tool was used for these calculations as incorporated in the Amsterdam Density Functional (ADF) package. The Geometry of the FeO structure was optimized by using the LDA and GGA method. Geometric optimization is optimized at iteration 90, the maximum force is 0.27 eV/Å and the maximum energy is equal to 0.27 eV The CAPZ (Ceperley–Alder–Perdew–Zunger) and PBE (Perdew–Burke–Ernzerhof) functionals were carried out for the exchange correlation potential as incorporated in the LDA and GGA, respectively. Density functional theory underestimates the electronic properties of transition metal oxides due to a lack of consideration of the onsite Columbic repulsion between the 3d electrons of the metal. Therefore, in order to avoid this problem, the Hubbard potential (U) is used to overcome the underestimation [12]. An optimized value of 0.6 eV of the Hubbard potential was used (after applying a range of 0.1–1 eV, as shown in Fig. 3) for further investigations of band structure and the DOS. After geometric optimization with the BAND code, the crystal structure of iron oxide is obtained.

3. Results and discussion

Fig. 1 confirms the cubic crystal structure for iron oxide, which is the stable structure for FeO at ambient conditions [6]. This is also known as the B1 (NaCl) type crystal structure [14]. A bond length between iron and oxygen of 2.2 Å is observed after geometric convergence for this cubic structure, which is in accordance with the reported value of the bond length [15].

To get the optimized lattice parameter, a slight variation in the value of the lattice parameter was done to get the minimum value of the formation energy for each varied lattice parameter. The formation energy versus unit cell volume calculated for each value of the lattice parameter is calculated and is plotted in Fig. 2. It was observed that for a=4.330 Å the system gets the lowest formation energy per atom (~4.2964 eV) which indicated the stability of the structure and is also in accordance with the experimentally reported value [16]. After this optimization, a=4.330 Å was used for all calculations. After getting the geometry optimization for the stable structure the band structure calculations and density of states were investigated both for the LDA and GGA.

With the addition of the Hubbard potential to simple LDA and GGA calculations a re-establishment of the band gap with respect to the ground state of the wüstite is observed. This results in the precise description of the electron-electron interaction in iron [8].

Different researchers used different values for the Hubbard potential to get different properties such as Wang et al. [12] who applied 3 eV, while Schron and Bechstedt [17] used U= 4 eV as the Hubbard potential. U= 3.5 eV Torres et al. [18] reported the use of 3.5 eV as the Hubbard potential to get an improved band gap. By keeping all other input parameters constant, we have varied different values of the Hubbard potential from 0.1 to 1 eV, and the observed band gap for wüstite due to these variations is given as in Fig. 3.
3.1. Electronic properties by LDA

The band structures calculated using the LDA and LDA+U are plotted in Fig. 4 (a) and (b), respectively. In Fig. 4 (a and b), the Fermi level is at 0 for both the LDA and LDA+U calculations as shown by the black dotted line at \( y=0 \). Spin up, i.e. the majority spin, is represented by the red color while the blue color indicates spin down, i.e. the minority spins.

From Fig. 4(a), it is observed that the band gap for FeO is zero, which is a result of the underestimation of the electron-electron interaction of the 3d electrons of iron in wüstite [19,20]. This results in the metallic nature of wüstite [4]. In order to correct for this underestimation of the DFT, the Hubbard potential \((U)\) can be added to the LDA. This results in the LDA+U method [21]. Applying the Hubbard potential to the LDA makes it a simple method to get an improved explanation of the ground state of the correlated systems. On the basis of these advantages along with low computational cost, this methodology has gained wide attention in the ab-initio calculation community [8].

Fig. 4(b) shows the band gap of 2.08 eV after applying the Hubbard potential of 0.6 eV to the LDA. The partial and total density of states for the LDA and LDA+U are plotted in Fig. 5(a) to (d).
Fig. 3. Variation of the band gap with the applied Hubbard potential using the LDA and GGA.

Fig. 4. Band structure of FeO by (a) LDA (b) by LDA+U.

Table 1
Comparison of values of the band gap energy using the GGA+U and the LDA+U (U = 0.6 eV).

<table>
<thead>
<tr>
<th>Used approximation in ADF</th>
<th>Used exchange correlational potential</th>
<th>Applied potential (eV)</th>
<th>Obtained band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our calculations</td>
<td>ADF (LDA)</td>
<td>PBE</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>ADF (GGA)</td>
<td>PBE</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>VASP [22]</td>
<td>PBE</td>
<td>6</td>
</tr>
<tr>
<td>Literature theoretical</td>
<td>VASP (GGA) [4]</td>
<td>PBE+U</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>VASP [7]</td>
<td>PAW</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>VASP [24]</td>
<td>PAW</td>
<td>5</td>
</tr>
<tr>
<td>Literature experimental</td>
<td>[4]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1. Electronic properties of FeO by the GGA

The criterion for the selection of the exchange correlational potential is based on different parameters such as on its accuracy for the calculation of the ground state properties of the material, specifically the magnetic moment of the transition metal, its lattice constants and its bulk modulus etc. [22]. Hence it is important to study the effect of the exchange correlational potential on the structural and electronic properties of FeO.

It is observed from Fig. 3 that an improved band gap for wüstite is observed for U = 0.6 eV. Hence this optimized value of the Hubbard potential was used for further optimization of the exchange correlational potential in the case of the GGA.
From Fig. 6 it is observed that the best value for the band gap of FeO is obtained for the PBE in the case of the GGA+U, so in all calculations the PBE is used as the exchange correlational potential.

The metallic nature for FeO is also observed for the GGA, as at ambient conditions the insulating ground state cannot be obtained by using the simple approximations in the DFT [23]. This problem of the wrong description for the electronic structure, especially the electronic band gap, is observed while dealing with transition metal based materials (like wüstite) using density functional theory with the LDA and GGA [19]. The band structures calculated by the GGA and GGA+U (by applying 0.6 eV as the value of the Hubbard potential) are given in Fig. 7(a) and (b), respectively. While all calculations for the GGA are performed using the optimized exchange correlational potential of PBE.
The red color indicates the majority spins (spin-up) and the blue color indicates the minority spins (spin-down) in Fig. 7(a) and (b). A gray line shows the line segment. In accordance with the crystal field theory, the splitting of the 3d band of iron into two sub-bands, i.e. t2g and eg is observed, where t2g is triply degenerate and eg is doubly degenerate [23]. A band gap of 2.34 eV is observed from Fig. 7(b), after applying the Hubbard potential of 0.6 eV to the GGA.

The total and partial density of states is calculated by the GGA+U. Fig. 8(a) and (b) show the partial and total density of states calculated by the GGA while Fig. 8(c) and (d) show the GGA+U calculations.

The top of the valance band is occupied by the 2p states of oxygen in Fig. 8(c). Antiferromagnetic behavior of wüstite is observed from Fig. 6(d), which is in accordance with the experimentally obtained magnetic behavior of wüstite [7].
By applying the Hubbard potential of 0.6 eV an improved band gap, i.e. 2.08 and 2.34 eV for the LDA+U and the GGA+U, is observed, respectively. Band gap values obtained at 0 K by the LDA+U, GGA+U and from the literature for comparison are given in Table 1, and it can be seen that the band gap energy of 2.34 eV obtained in our calculations by using the GGA+U is in good agreement with the experimental obtained band gap value, i.e. 2.4 eV, of FeO [4].

Conclusion

Density functional theory was used to investigate the structural and electronic properties of FeO. The BAND code is used in the ADF software. The effect of the Hubbard potential U on the LDA and GGA approximations was investigated. Geometric optimization was achieved by using the TZP as the basis set along with the PBE as the exchange correlation potential. The calculation of the lowest formation energy for FeO with lattice parameter 4.33 Å was obtained for the stable cubic crystal structure. The band structure for the GGA and LDA calculations showed the metallic nature of FeO. The partial and total density of states for these calculations was also in agreement with the observed band structure. To get the improved results, the Hubbard potential was applied after optimization from a range of 0.1 to 1 eV. With a low value of the Hubbard potential (0.6 eV), an improved band gap of 2.34 eV and 2.08 eV was observed for the GGA+U and LDA+U calculations, respectively. This is in good agreement with the experimentally reported value of the band gap for FeO, i.e. 2.4 eV Antiferromagnetic behavior for the GGA+U was also observed from the obtained density of states. From these calculations, it was observed that the GGA+U gives more accurate results, as compared to the LDA+U. Hence, the Amsterdam density functional (ADF) program can be used to get improved electronic properties with a relatively lower value of the Hubbard potential in the generalized gradient approximation, which gives reproducible results at low computer cost. A low value of Hubbard potential is used for the first time to get improved and repeatable results in ADF program with the BAND code.

Acknowledgment

One of the authors (R. Ashraf) would like to thank Dr. Tariq Mahmood, Government College Women University, Sialkot for guidance about this research work. This research did not receive any specific grant from funding agencies in the public, commercial, or non-profit sectors.

References