Electro-Optic And Magneto-Dielectric Properties Of Multifunctional Nitride And Oxide Materials

Ambesh Dixit
Wayne State University

Follow this and additional works at: http://digitalcommons.wayne.edu/oa_dissertations
Part of the Condensed Matter Physics Commons, and the Materials Science and Engineering Commons

Recommended Citation

This Open Access Dissertation is brought to you for free and open access by DigitalCommons@WayneState. It has been accepted for inclusion in Wayne State University Dissertations by an authorized administrator of DigitalCommons@WayneState.
ELECTRO-OPTIC AND MAGNETO-DIELECTRIC PROPERTIES OF MULTIFUNCTIONAL NITRIDE AND OXIDE MATERIALS

by

AMBESH DIXIT

DISSERTATION

Submitted to the Graduate School of Wayne State University, Detroit, Michigan

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

2010

MAJOR: PHYSICS

Approved by:

Advisor

Date

Co-advisor

Date
DEDICATION

“TO MY TEACHERS DR GAVIN LAWES AND DR RATNA NAIK”
ACKNOWLEDGEMENTS

I would like to express my heartiest gratitude to all who contributed directly or indirectly to make this work possible. First I would like to thank my advisor Dr. Gavin Lawes for his willingness to have me as his Ph.D. student. His constant guidance, motivation, discussions during this whole work were remarkably helpful to shape numerous work into wonderful results. I learned a lot both scientific and non-scientific things from him. Second, I would like to express my sincere gratitude to my co-advisor Dr. Ratna Naik, who introduced me to my advisor and helped in establishing my Ph.D. carrier. I learned a lot from her. Her valuable suggestions and enormous discussion about future opportunities and professional developments will be very useful and helpful in taking decisions at various situations. I am very fortunate to have both as my advisor and co-advisor for my thesis work and giving me freedom to do whatever I wanted to explore.

In addition, I would like express my sincere thanks to Dr. Jagdish S. Thakur, Dr. Caroline Morgan and Dr. Gregory W. Auner for their willingness to serve as committee members for my Ph.D. thesis. I learned a lot from Dr. Jagdish S. Thakur, especially the optical and electronic properties and their correlation with intrinsic defects present in semiconductor systems.

I would like to thank Dr. Vaman Naik. I learned a lot especially about nitride semiconductors and numerous characterization techniques such as Raman spectroscopy. The scientific discussions with him and Dr. Jagdish S Thakur on optical properties of semiconductors provided an indepth understanding of the subject.

My special thanks to Dr. Sudakar Chandran and Dr. M. B. Sahana for their help during this work. I greatly appreciate help from Dr. Sudakar Chandran, who taught me almost all the growth and characterization techniques used during this work. Without his constant help and support during late hours in the lab, it would have been more difficult to work out things. In addition I would like to thank Dr. Boris Nadgorny, Dr. Raghava Panguluri, Dr.
A. B. Harris, Dr. Ram Seshadri, Dr. M. A. Subramanian, Dr. R. Suryanarayanan and Dr. M. S. Rao for their support/discussion during numerous collaborative work.

I wish to thank my seniors Dr. Parsu Ram Kharel and Dr. Ronald J. Tackett for their help and support in lab, my lab mates Mr. Akila Kumarasiri, Mr. Rajesh Regmi. I also express my sincere thanks to co-workers Mr. B. Ramchandran, Mr. Brajesh Tiwari, Mr. Pushkal Thapa, Dr. Andrew E. Smith and Dr. Brent C. Melot for interesting collaborative work. I sincerely appreciate the companionship of my friend Mr. Abhishek Sundararajan during his WSU stay and having wonderful technical and non-technical discussions. I am also thankful to my brother Mr. Pankaj Dixit for his constant encouragement at every moment. I missed both Mr. Abhishek Sundararajan and Mr. Pankaj Dixit, a lot.

Above all, I am thankful to my mother Smt. Gayatri Dixit and father Sri B. P. Dixit, who taught me how to read, write and work hard. I have no words to express my feelings of indebtedness to them.
Contents

DEDICATION ................................................................. ii
ACKNOWLEDGEMENTS ................................................... iii
LIST OF TABLES .......................................................... xi
LIST OF FIGURES .......................................................... xii

1 INTRODUCTION -GENERAL OVERVIEW 1
  1.1 INTRODUCTION ...................................................... 1
  1.2 COMPOUND SEMICONDUCTORS .................................... 4
      1.2.1 NITRIDE COMPOUND SEMICONDUCTORS .................... 5
      1.2.2 OXIDE COMPOUND SEMICONDUCTORS ....................... 6
  1.3 MULTIFUNCTIONAL OXIDE MULTIFERROICS ....................... 7

2 MULTIFUNCTIONAL MATERIALS -THEORETICAL AND EXPERIMENTAL REVIEW (DIFFICULTIES AND CHALLENGES) 8
  2.1 SEMICONDUCTORS AND THEIR CLASSIFICATIONS .................. 8
  2.2 MULTIFUNCTIONAL MAGNETIC SEMICONDUCTORS .................. 14
  2.3 ORIGIN OF MAGNETISM AND SPIN POLARIZATION IN DILUTE MAGNETIC SEMICONDUCTORS ......................... 16
      2.3.1 ZENER MODEL ................................................. 17
      2.3.2 RUDDERMAN-KITTEL-KASUYA-YOSIDA (RKKY) MODEL .... 18
      2.3.3 MEAN FIELD ZENER MODEL ................................. 20
2.3.4 ZENER DOUBLE EXCHANGE MODEL .................................. 20
2.3.5 BOUND MAGNETIC POLARON (BMP) MODEL ...................... 21
2.3.6 $d^0$ MODEL-MAGNETISM IN SYSTEMS WITHOUT MAGNETIC IMPURITY DOPANTS ................................. 25
2.3.7 CHARGE TRANSFER FERROMAGNETISM-A MECHANISM FOR DEFECT-RIDDEN OXIDE SYSTEMS .................. 26
2.4 MULTIFUNCTIONAL MULTIFERROICS .................................... 27
2.5 TYPES OF MULTIFERROICS AND MICROSCOPIC ORIGIN OF MULTIFERROICITY ........................................ 31
2.6 MICROSCOPIC ORIGIN OF FERROELECTRICITY, MAGNETISM, AND MAGNETOELECTRIC COUPLING IN TYPE-I MULTIFERROICS ....... 32
2.6.1 PARAMAGNETIC DOPING ........................................... 32
2.6.2 LONE PAIR ASYMMETRY ......................................... 33
2.6.3 ELECTRONIC FERROELECTRICITY (CHARGE ORDERING) ... 33
2.6.4 GEOMETRICALLY DRIVEN FERROELECTRICITY ............... 34
2.7 MICROSCOPIC ORIGIN OF FERROELECTRICITY, MAGNETISM, AND MAGNETOELECTRIC COUPLING IN TYPE-II MULTIFERROICS ..... 35
2.7.1 MULTIFERROICS WITH SPIRAL MAGNETIC STRUCTURE ....... 35
2.7.2 MULTIFERROICS WITH COLLINEAR MAGNETIC STRUCTURE 40
2.8 TWO PHASE MULTIFERROICS ........................................... 42

3 III-NITRIDES AND RELATED DILUTE MAGNETIC SEMICONDUCTORS (DMSs) - OPTICAL, ELECTRONIC AND MAGNETIC PROPERTIES 43
3.1 INTRODUCTION .............................................................. 43
3.2 EXPERIMENTS AND RESULTS ............................................ 54
    3.2.1 FABRICATION OF InN, In$_{1-x}$Ga$_x$N and In$_{1-x}$Cr$_x$N THIN FILMS 54
3.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF InN AND In$_{1-x}$Cr$_x$N THIN FILMS .......................................................... 56
3.2.3 PHASE SEPARATION AND OPTICAL PROPERTIES IN OXYGEN RICH InN THIN FILMS .............................................................. 60
3.2.4 STRONG PLASOM ABSORPTION IN RF SPUTTERED InN THIN FILMS ......................................................................................... 66
3.2.5 PHONON MODES, $E_1$(LO) PHONON-PLASMON COUPLED MODES, AND CRITICAL POINTS IN INDIUM GALLIUM NITRIDE (In$_{1-x}$Ga$_x$N) THIN FILMS ............................................ 73
3.2.6 ROOM TEMPERATURE MAGNETIC PROPERTIES AND SPIN POLARIZATION IN In$_{1-x}$Cr$_x$N THIN FILMS ........................... 80
3.3 CONCLUSION .................................................................................. 88

4 INDIUM OXIDE COMPOUND SEMICONDUCTOR - OPTICAL, ELECTRONIC AND MAGNETIC PROPERTIES 90
4.1 INTRODUCTION .................................................................................. 90
4.2 EXPERIMENTS AND RESULTS ............................................................ 93
  4.2.1 FABRICATION OF INDIUM OXIDE (In$_2$O$_3$) THIN FILMS ........... 93
  4.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF In$_2$O$_3$ THIN FILMS .................................................................. 94
  4.2.3 PERSISTENT PHOTOCONDUCTIVITY (PPC) IN In$_2$O$_3$ THIN FILMS .............................................................................. 97
  4.2.4 TRANSPORT AND OPTICAL PROPERTIES OF VACUUM ANNEALED In$_2$O$_3$ THIN FILMS ......................................................... 100
  4.2.5 CATION AND ANION VACANCY DEFECTS AND THE ONSET OF FERROMAGNETISM IN VA In$_2$O$_3$ THIN FILMS ................. 104
4.2.6 STRONG PLASMON OBSERVATION AND THEIR SWITCHABILITY IN In$_2$O$_3$ THIN FILMS ........................................ 111
4.3 CONCLUSION ............................................................................................................. 115

5 YMn$_{1-x}$In$_x$O$_3$ MULTIFERROIC -MAGNETIC, THERMAL AND MAGNETODIELECTRIC PROPERTIES 116
5.1 INTRODUCTION ........................................................................................................ 116
5.2 EXPERIMENTS AND RESULTS .................................................................................. 118
  5.2.1 SYNTHESIS OF BULK YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES .................. 118
  5.2.2 STRUCTURAL CHARACTERIZATION OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES ................................................................. 118
  5.2.3 MAGNETIC AND THERMAL PROPERTIES OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES ................................................................. 119
  5.2.4 DIELECTRIC AND MAGNETODIELECTRIC PROPERTIES OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES ................................................................. 122
5.3 CONCLUSION ............................................................................................................. 125

6 Ni$_3$V$_2$O$_8$ MULTIFERROIC -ELECTRONIC, DIELECTRIC, AND MAGNETODIELECTRIC PROPERTIES 126
6.1 INTRODUCTION ........................................................................................................ 126
6.2 EXPERIMENTS AND RESULTS .................................................................................. 129
  6.2.1 SYNTHESIS OF Ni$_3$V$_2$O$_8$ BULK CERAMIC, SINGLE CRYSTAL AND THIN FILMS ................................................................. 129
  6.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF Ni$_3$V$_2$O$_8$ THIN FILMS ................................................................. 130
  6.2.3 COMPOSITION, OPTICAL AND ELECTRONIC PROPERTIES ............... 134
6.2.4 ELECTRIC AND MAGNETIC FIELD CONTROL OF MULTIFERROIC TRANSITION IN Ni₃V₂O₈ SYSTEM .......................... 138
6.2.5 DIELECTRIC CRITICAL BEHAVIOUR AT MULTIFERROIC TRANSITION TEMPERATURE FOR Ni₃V₂O₈ SYSTEM ........ 142
6.3 CONCLUSION ................................................................. 144

7 FeVO₄ MULTIFERROIC - A NEW MULTIFERROIC IN VANADATE FAMILY .............................. 146

7.1 INTRODUCTION ............................................................... 146
7.2 EXPERIMENTS AND RESULTS ............................................. 147
    7.2.1 SYNTHESIS OF FeVO₄ BULK CERAMIC AND THIN FILM SAMPLES .................................................. 148
    7.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF BULK AND THIN FILM FeVO₄ SAMPLES ............. 149
    7.2.3 ELEMENTAL, ELECTRONIC AND OPTICAL PROPERTIES ................................................................. 152
    7.2.4 MAGNETIC AND THERMAL PROPERTIES OF FeVO₄ BULK CERAMIC SAMPLES ...................................... 156
    7.2.5 DIELECTRIC AND FERROELECTRIC PROPERTIES ................................................................. 159
    7.2.6 MAGNETODIELECTRIC COUPLING IN BULK FeVO₄ CERAMIC SAMPLES ............................................. 165
    7.2.7 MAGNETODIELECTRIC PROPERTIES AND ELECTRIC AND MAGNETIC FIELD CONTROL OF MULTIFERROIC TRANSITION 166
7.3 CONCLUSION ................................................................. 171

8 CONCLUSIONS ................................................................. 172

Appendix A ................................................................. 177
    .1 Energy band model ..................................................... 177
List of Tables

1.1 Semiconductor periodic table ................................................. 4
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic energy band diagram for insulators, semiconductors and metals [30]</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic E-k diagram for (a) direct bandgap semiconductor and (b) indirect bandgap semiconductors</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic E-k representation of non-degenerate and degenerate semiconductors [13]</td>
<td>12</td>
</tr>
<tr>
<td>2.4</td>
<td>A schematic representation of (a) a non-magnetic and (b) a dilute magnetic semiconductor [31]</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>A schematic representation of (a) AFM coupling between two adjacent localized transition metal (TM) cations mediated by a shared anion and (b) FM coupling between localized TM d-electrons mediated by electron charge carriers</td>
<td>17</td>
</tr>
<tr>
<td>2.6</td>
<td>RKKY exchange parameter J(r) oscillations as a function of r, the distance from a magnetic ion</td>
<td>19</td>
</tr>
<tr>
<td>2.7</td>
<td>Curie temperature for different p-type semiconductor containing 5% Mn [23]</td>
<td>21</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic representation of the double exchange interaction between adjacent Co^{2+} ions leading to ferromagnetic coupling</td>
<td>22</td>
</tr>
<tr>
<td>2.9</td>
<td>Schematic representation of the polaron pair model, indicating an interstitial region [44]</td>
<td>23</td>
</tr>
</tbody>
</table>
2.10 Schematic representation of a bound magnetic polaron (BMP). Cations are represented by small circles and unoccupied oxygen sites are represented by squares, indicating an interstitial [45].

2.11 Schematic representation of charge transfer magnetism; electron transfer between the charge reservoir and the defect band can satisfy the Stoner criterion leading to ferromagnetic splitting [37].

2.12 Schematic representation of magnetic, ferroelectric, linear magnetoelectric, magneto-dielectric, and multiferroic systems.

2.13 Schematic representation of the microscopic mechanism of spin induced polarization for the spin current model [84].

2.14 Schematic representation of the change of local electric polarization induced by spin canting (a) in clockwise and (b) counterclockwise spiral spin structure and (c) spin canting AF spin structure [87].

2.15 Fig (a) the magnetically induced polarization is zero for sinusoidal spin structure and (b) non-zero polarization $\vec{P}$ is induced perpendicular to both the spin rotation axis $\hat{e}_3$ and the spin wave vector $\vec{Q}$ for the non-collinear spin structure [85].

2.16 Schematic representation of the polarization $\vec{P}$ induced by simultaneous charge ordering and and dimer type Ising spin chain. Exchange striction shifts cations away from their centrosymmetric positions [77].

3.1 Bandgap energies of In$_{1-x}$Ga$_x$N system over the entire solar spectrum. Conventional MJ solar cell materials Ge, GaAs and GaInP gap energies are shown in the right-hand panel for comparison [22].

3.2 Schematic representation of the wurtzite III-N crystal structure, where yellow spheres represent group III-element and gray spheres represent N atoms [98].
3.3 Stick and ball model of wurtzite and zinc blende crystal structures. Figures at the bottom indicate the projections onto the (0001) and (111) planes for wurtzite and zinc blende respectively [99].

3.4 Energy bandgap versus in-plane lattice constant of III-nitrides and other semiconductors [99].

3.5 (a) Peak saturation velocities for Wurtzite III-nitrides [2] and (b) bandgap energy vs Fermi level stabilization energy ($E_{FS}$) [104].

3.6 Growth condition for InN thin films deposition.

3.7 XRD pattern for (a) InN-metal film and (b) InN-oxide film. “*” indicates the peaks due to the Al$_2$O$_3$ (0006) reflection. HRTEM images of (c) InN-metal and (d) InN-oxide thin films. In (c)“G” shows the grain boundary region between the highly oriented InN columnar crystals. In (d) areas marked with letters “a” and “c” indicate the disordered amorphous and crystalline regions within the InN crystallites.

3.8 (a) XRD pattern for InN thin films having the lowest (top panel) and highest (lower panel) carrier concentrations. “*” indicates the peak due to the Al$_2$O$_3$ (0006) reflection. The small anomaly in the top panel near 35° represents an instrumental error. (b) Cross-sectional SEM micrograph of InN/Sap thin film. HRTEM images of (c) the lowest and (d) highest carrier concentration InN thin films.

3.9 XRD pattern of In$_{0.098}$Cr$_{0.02}$N/Sap (bottom panel) and In$_{0.095}$Cr$_{0.05}$N/Sap (top panel).

3.10 X-ray photoelectron spectrum (XPS) of In3d$_{5/2}$ after 10 nm etching for (a) InN-metal and (b) InN-oxide thin films. O1s spectrum for the (a) and (b) are shown in (c) and (d). The atomic (%) concentration of In, N and O below the surface of (e) InN-metal and (f) InN-oxide films.
3.11 Raman spectra of (a) InN-metal and (b) InN-oxide thin films. "*" indicates modes at 219 and 303 cm\(^{-1}\) from In\(_2\)O\(_3\). Reflection spectra for InN films (a) and (b) are shown in (c) and (d). The solid curve is experimental data and the dashed curve is theoretical fit. The insets to (c) and (d) show the photoluminescence spectra, which exhibit broad peaks near 1.85 eV corresponding to the optical absorption edge of the samples. The sharp feature at 1.8 eV in the inset to (d) is due to the sapphire substrate, while the sharp peak at 2.4 eV is the first order Raman spectrum signal.

3.12 (a) RBS spectra for highest carrier concentration InN/Sap thin film with a standard detector of 140° angle (red circle), 180° annular detector (blue square) and 30° annular detector (black triangle). The solid line is the NDF simulation fit to the experimental data. (b) Raman spectrum of the InN thin films having lowest carrier concentration (top panel) and highest carrier concentration (bottom panel). "*" indicates mode at 219 and 303 cm\(^{-1}\) from In\(_2\)O\(_3\). (c) Optical reflectance spectra of InN/Sap thin films (top panel) and absorption spectra (bottom panel). Closed (open) symbols and dotted (dashed) lines show the experimental data and simulated spectrum for the film having a carrier concentration of 1.26 \(\times\) 10\(^{21}\) cm\(^{-3}\) (3.84 \(\times\) 10\(^{20}\) cm\(^{-3}\)) and (d) normalized plot of \(\text{Im}(\frac{-1}{\epsilon(w)})\) vs \(w_p\) plot for different InN/Sap thin films, where the arrows indicate the corresponding \(w_p\) values.

3.13 (a) IR reflectance spectra of In\(_{1-x}\)Ga\(_x\)N (x = 0, 0.15, 0.30 and 0.54) thin films under normal incidence. The dashed curves are the corresponding theoretical simulated reflectance curves. (b) variation of critical point energies of In\(_{1-x}\)Ga\(_x\)N samples as a function of x. The solid lines show the fitted data.
3.14 Raman spectra of In$_{1-x}$Ga$_x$N ($x = 0, 0.15, 0.30$ and $0.54$) thin films using (a) red laser (1.58 eV) excitation source, (b) green laser (2.41 eV) excitation source. The dashed lines represent the variation of E$_2$(low), A$_1$(LO) and its replica 2A$_1$(LO) mode energy variation with increasing Ga atomic fraction. (c) the energy variation of 1A$_1$(LO), 2A$_1$(LO), E$_2$(low) and E$_2$(high) modes with respect to Ga atomic fraction and (d) energy variation in the ration of A$_1$(LO)/E$_2$(high) with respect to the Ga atomic fraction for In$_{1-x}$Ga$_x$N thin films.

3.15 Curie temperature for various III-V semiconductor compounds, containing 5% Mn per cation in 2+ charge state and $3.5 \times 10^{20}$ holes cm$^{-3}$. [23]

3.16 ($(\alpha * E)^2$) versus energy for (a) In$_{0.98}$Cr$_{0.02}$N and (b) In$_{0.95}$Cr$_{0.05}$N thin films. The red line is an extrapolation to the linear region for optical absorption edge and the lower energy peak $\sim 0.7$ eV is the plasmon absorption peak for both the films. (c) Raman spectrum for In$_{0.98}$Cr$_{0.02}$N (bottom panel) and In$_{0.95}$Cr$_{0.05}$N (top panel) thin films where “*” corresponds to the peaks from the 128 and 305 cm$^{-1}$ modes from In$_2$O$_3$ and (d) the temperature dependence resistivity for In$_{0.98}$Cr$_{0.02}$N and In$_{0.95}$Cr$_{0.05}$N thin films.

3.17 Room temperature photoluminescence for In$_{0.98}$Cr$_{0.02}$N and (b) In$_{0.95}$Cr$_{0.05}$N thin films.

3.18 (a) Temperature dependent magnetization for an In$_{0.95}$Cr$_{0.05}$N thin film. (b) Field dependent magnetization at 15 K (red triangles) and 300 K (black circles) for an In$_{0.95}$Cr$_{0.05}$N/Sap thin film. (c) Temperature dependent magnetization for an In$_{0.98}$Cr$_{0.02}$N thin film and (d) field dependent magnetization at 15 K (red triangles) and 300 K (black circles) for an In$_{0.98}$Cr$_{0.02}$N/Sap thin films. The substrate background was subtracted for both samples and the respective unprocessed data is shown in the inset.
3.19 Normalized conductance curves for superconducting Nb contacts with (a) \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and (b) \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) thin films. The solid red lines show simulated fits to the experimental data obtained using the diffusive model. 

4.1 (a) \( \text{In}_2\text{O}_3 \) cubic bixbyite crystal structure and (b) non equivalent b and d In cation sites and O vacancies in \( \text{In}_2\text{O}_3 \).

4.2 Bottom panel: XRD spectrum for as grown \( \text{In}_2\text{O}_3/\text{Sap} \) thin film and Top panel: XRD spectrum for vacuum annealed \( \text{In}_2\text{O}_3/\text{Sap} \) thin film with insets showing their XRD patterns in logarithmic scale.

4.3 (a) Cross-sectional SEM of an as grown \( \text{In}_2\text{O}_3 \) film on a silicon substrate and (b) HRTEM image of an \( \text{In}_2\text{O}_3 \) film with misfit or edge dislocations, marked by arrows. Inset: Fast Fourier transform of the image indicating the fourfold symmetry of \( \text{In}_2\text{O}_3 \).

4.4 Room temperature Raman spectra for \( \text{In}_2\text{O}_3 \) thin films on (100) MgO, (1102) r-axis \( \text{Al}_2\text{O}_3 \), (0001) c-axis \( \text{Al}_2\text{O}_3 \) substrates and \( \text{In}_2\text{O}_3 \) bulk powder sample, from bottom to top panel respectively. The corresponding Raman spectra for different substrates are shown with red curves in the respective panels.

4.5 (a) Sharp resistance changes observed upon illumination of an \( \text{In}_2\text{O}_3 \) thin films with a high intensity (\( \sim 225\text{mW/cm}^2 \)) UV LED at 365 nm, with some sample to sample variation lying within the limits indicated by the two curves from samples A and B. Inset shows the results of an \( \text{In}_2\text{O}_3 \) film to the red, green and UV LEDs, with nearly same intensity. (b) Change in resistance of \( \text{In}_2\text{O}_3 \) thin film with different UV LED incident power, as indicated with applied voltage at the corresponding time in the plot.
4.6 (a) Optical absorption $(\alpha \ast E)^2$ versus E for the In$_2$O$_3$ thin film before (red circles) and after (blue circles) UV irradiation. The dashed lines indicate the optical absorption edges. (b) Time decay of the conductance of In$_2$O$_3$ thin film at different temperatures: 200 K, 275 K, 300 K, 325 K and in air (at 300 K). The dashed lines show fits to stretched exponentials. The solid line shows a fit to the logarithmic relaxation.

4.7 (a) UV-Vis-NIR transmission and reflection spectra for as grown and vacuum annealed In$_2$O$_3$/Sap thin films. (b) Optical absorption $(\alpha \ast E)^2$ versus energy E for as grown and vacuum annealed In$_2$O$_3$/Sap thin films.

4.8 Resistivity of the as grown and vacuum annealed In$_2$O$_3$/Sap thin films. The resistivity for the as grown film is plotted on a logarithmic scale, as shown on the left y-axis.

4.9 M(H) curves for as grown (closed blue circles) and vacuum annealed (open red circles) In$_2$O$_3$/Sap thin films (corrected for diamagnetic contributions). The bottom right inset shows the unprocessed data. The top left inset shows the magnetization curves of bare vacuum annealed sapphire.

4.10 Rutherford backscattering plots for (a) as grown (b) vacuum annealed In$_2$O$_3$/Sap thin films. The red lines show theoretical simulations.
4.11 High-resolution TEM micrographs of 100 surface regions for (a) as grown (AG) and (b) vacuum annealed (VA) In₂O₃ samples. (c) A magnified view of a section of (b) with arrows showing distortions in the crystal lattice. The square region of the HRTEM image in (c) corresponds to a unit cell of In₂O₃ shown in the ball and stick model projected along (100) plane. The inset ((i) and (ii)) in (c) are the simulated HRTEM images with (i) a oxygen vacancy and (ii) a oxygen vacancy with two adjacent In atoms clustering model. (d) HRTEM image of high VA In₂O₃ just below amorphous surface region. The top of surface is highly defective compared to the bulk (∼10 nm below surface). The short arrows indicate the dark region, showing typical In clustered regions. The long arrow shows an edge dislocation.

4.12 (a) Optical absorption (α * E)² versus energy for as grown (AG), vacuum annealed (VA) and re air annealed (RAA) In₂O₃/Sap thin films. (b) Optical absorption spectrum plotted on a reduced scale to show the plasmon peak near 0.5 eV in VA In₂O₃/Sap.

4.13 Room temperature photoluminescence (PL) spectrum for as grown (AG), vacuum annealed (VA) In₂O₃/Sap thin films and a bare sapphire substrate, collected using a 514.5 nm wavelength excitation source. The spectrum near 2.4 eV show the 1ˢᵗ order Raman spectrum of respective samples. The insets showing schematic energy diagram for AG and VA In₂O₃ thin films with oxygen vacancy states ∼1.9 eV for the VA In₂O₃ thin film.

5.1 YMnO₃ crystal structure with trigonal bipyramids representing MnO₅ polyhedra and gray spheres represent Y ions. (a) a stack of two consecutive MnO₅ layers and the sandwiched Y layer, looking down the c axis in the paraelectric phase and (b) A view of the ferroelectric phase from perpendicular to the c-axis, showing the layered nature of YMnO₃ [69].
5.2 (a) XRD pattern for YMn$_{1-x}$In$_x$O$_3$ samples, as indicated by legend on the right of the figure. (b) and (c) Vegard’s law plots for YMn$_{1-x}$In$_x$O$_3$ showing the systematic change in lattice parameter with In content .......................... 119

5.3 (a) Temperature dependent magnetic susceptibility at $\mu_0H = 0.5T$ for YMn$_{1-x}$In$_x$O$_3$ samples with the inset showing the background corrected susceptibility for $x=0$ and $x=0.25$ samples. (b) C/T versus T, for YMn$_{1-x}$In$_x$O$_3$ samples. .......................... 120

5.4 (a) Relative change in capacitance versus temperature for YMn$_{1-x}$In$_x$O$_3$ samples, with the dashed arrow indicating the dielectric anomalies associated with AFM ordering transitions. (b) Magnetic field dependence of the capacitive response with solid bars on the $x=0$, 0.5 and 0.75 curves indicating the scatter in the data before smoothing. The dashed line on the $x=0.75$ curve is the best fit. (c) Temperature dependence of the magnetocapacitive coupling constant for the $x=0.5$ and $x=0.75$ YMn$_{1-x}$In$_x$O$_3$ samples. (d) Temperature dependence of the AFM ordering transition on $x$ in YMn$_{1-x}$In$_x$O$_3$, extracted from different measurements. .............................................. 123

6.1 (a) Schematic orthorhombic Ni$_3$V$_2$O$_8$ crystal structure with Ni sublattice. There are two inequivalent sites for the Ni$^{2+}$ ions, spine Ni$^{2+}$ (red sphere) and cross-tie Ni$^{2+}$ (yellow sphere). The schematic spin arrangement in the antiferromagnetic (b) HTI, (c) LTI, and (d) CAF phases. In Fig (b), (c) and (d), the blue arrow corresponds to the yellow sphere of Fig (a) for cross-tie Ni$^{2+}$ sites .............................................. 127

6.2 The $\theta-2\theta$ XRD pattern for Ni$_3$V$_2$O$_8$ thin films on (0001) sapphire (top panel) and n-type conducting (100) silicon (lower panel) ......................... 131

6.3 The representative surface SEM micrograph, with inset showing cross-sectional SEM image for Ni$_3$V$_2$O$_8$/Sap thin film .......................... 133
6.4 The room temperature Raman spectrum for a Ni$_3$V$_2$O$_8$/Sap thin film (bottom panel) and a Ni$_3$V$_2$O$_8$ single crystal (top panel) 134

6.5 XPS spectra for (a) Ni and (b) V and O for Ni$_3$V$_2$O$_8$/Si thin films and (c) Ni and (d) V and O for a Ni$_3$V$_2$O$_8$ single crystal 135

6.6 The optical absorption $(\alpha \ast E)^2$ (left axis) and $(\alpha \ast E)^{1/2}$ (right axis) versus energy E for Ni$_3$V$_2$O$_8$/Sap thin films. The inset showing $(\alpha \ast E)^2$ versus energy E plot, exhibiting a strong absorption $\sim$1.3 eV, indicating a Ni d-d interband transition as schematically shown in the representative energy band diagram 136

6.7 The valence band spectrum for a Ni$_3$V$_2$O$_8$/Si film (top panel) and a Ni$_3$V$_2$O$_8$ single crystal (bottom panel) 137

6.8 (a) Dielectric constant versus temperature at $E = 0 = \mu_0H$ fields (bottom panel) and $E=25$ MV/m, $\mu_0H=0$ T (middle panel) and $E=25$ MV/m, $\mu_0H=8$ T (top panel) for Ni$_3$V$_2$O$_8$/Si thin film and (b) E-H-T phase diagram for Ni$_3$V$_2$O$_8$ near the HTI to LTI phase transition, where red triangles and blue circles represent the variation of $T_L$ with magnetic and electric fields with solid lines showing power law fits to the magnetic and electric field variation of $T_L$. 140

6.9 (a) Temperature dependence of the dielectric constant near multiferroic transition temperature $T_L$ of a Ni$_3$V$_2$O$_8$ single crystal, where the solid lines are fits to critical behaviour (b) Relative change in the dielectric constant of a Ni$_3$V$_2$O$_8$ single crystal versus reduced temperature $|t|$ at three different warming rates 0.1K/min (squares), 0.05K/min (triangles) and 0.01K/min (circles). The solid symbols indicate data above $T_L$ while open symbols indicate data below $T_L$. The dashed lines show the fits to critical behaviour. 143

7.1 (a) The chain structure of FeVO$_4$ consist of Fe-O polyhedra and (b) the form of a six-column doubly bent chain 147
7.2 XRD ($\theta - 2\theta$) pattern for (a) FeVO$_4$ bulk powder, where the expected peak positions are indicated by dashed lines (red) along the lower edge of figure. (b) FeVO$_4$ thin film ................................................................. 150

7.3 (a) Surface SEM micrograph (b) cross-sectional SEM image and (c) room temperature Raman spectrum on FeVO$_4$ bulk ceramic and thin film samples. The peak at 520 $cm^{-1}$ arises from the Si substrate ................................. 151

7.4 Elemental XPS spectrum of Fe (top panel) and V and O (lower panel) for FeVO$_4$ bulk ceramic ................................................................. 152

7.5 Optical absorption spectra ($\alpha*E^{1/2}$ versus E (right axis) and ($\alpha*E^2$) versus E (left axis) for FeVO$_4$/Sap thin films. The jump at 3.5 eV is due to the change in gratings at these wavelengths. The iron Fe$^{3+}$ ($d^5$) high spin electronic configuration in an octahedral coordination is shown in the inset. ........... 154

7.6 Valence band spectrum of FeVO$_4$ bulk ceramic, with the inset showing a schematic energy band diagram for FeVO$_4$ ................................. 156

7.7 (a) Magnetic and inverse magnetic susceptibility versus temperature for a FeVO$_4$ bulk ceramic measured at 100 Oe, where the dashed line is the high temperature Curie-Weiss fit to the magnetic data. (b) Magnetic susceptibility at H=100 Oe, 10 kOe and 50 kOe. ................................. 157

7.8 Temperature dependent heat capacity for FeVO$_4$ bulk ceramic at H=0 T plotted as: (a) C/T versus T and (b) C/T$^2$ versus T, where dashed line is the best fit at higher temperature to $C/T = \gamma T + \alpha T^3$. ........................................... 158

7.9 Bulk FeVO$_4$ sample polarization at poling fields E=±200 kV/m and H=0 Oe and for E=+200 kV/m with magnetic fields of H=10, 30, and 50 kOe. Inset: temperature dependence of the dielectric constant measured at H=0 and 50 kOe. ......................................................... 160
7.10 (a) Temperature dependent Raman spectra on FeVO$_4$ bulk ceramic. (b) % relative change of Raman shifts for the 498, 733, 842 and 928 cm$^{-1}$ modes with temperature. .................................................. 162

7.11 (a) Temperature dependent dielectric constant and resistivity for FeVO$_4$ bulk ceramic at H=0 T (b) Temperature dependence of dielectric constant near $T_{N1}$ (c) Temperature dependence of the dielectric constant at H=0, 20, 40, 50 and 80 kOe. .................................................. 164

7.12 Magnetic field dependence of the relative change in the dielectric constant for bulk FeVO$_4$ at different temperatures with a vertical offset included for clarity. The y-axis is labeled with the values for the T=14.5K measurement. 165

7.13 (a) Temperature dependent dielectric constant for FeVO$_4$ thin films at H=0 T with inset showing polarization measured at poling fields $E_{pole}=\pm$ 10 MV m$^{-1}$ (b) Temperature dependent dielectric constant measured at E=0 and E=3.75 MV m$^{-1}$ (background was subtracted for clarity). .................................................. 168

7.14 (left) Electric and magnetic field dependence of the multiferroic transition temperature $T_{N2}$ and (right) Magnetic field dependence of multiferroic transition temperature with the proposed magnetic field induced spin-reorientation crossover. NCI* indicates the proposed phase having a spin-reoriented structure.170

1 Schematic development of energy band diagram for silicon Si .......................... 178
2 Schematics explaining the sequential steps for solid state reaction technique . 180
3 Schematic of the experimental geometry for X-ray diffraction (Bragg’s Law) 186
Chapter 1

INTRODUCTION - GENERAL

OVERVIEW

1.1 INTRODUCTION

The push towards miniaturization and higher speeds in electronic devices has spurred a search for the identification and development of new multifunctional materials. Materials exhibiting more than a single electrical, optical, magnetic, elastic, or other characteristic response, are known as *multifunctional materials*. These materials provide the possibility of integrating multiple functional properties, along with entirely new properties arising from cross-coupling, into a single system. Such multifunctional materials can be classified into a large number of systems including compound semiconductors, dilute magnetic semiconductors, colossal magnetoresistive materials, and magneto-electric multiferroic materials. As a specific example of how multifunctional materials can be used to develop new devices, we consider new compound semiconductors for optoelectronic applications. Si, elemental semiconductor, was crucial for building the modern electronic industry. However Si is an indirect bandgap semiconductor and thus is not an efficient light emitter or absorber. Photovoltaic and optoelectronic devices require a strong interplay between photons and electrons.
Direct bandgap semiconductors are more suitable for such applications which show strong absorption or emission for the desired electromagnetic spectral range. III-V and II-VI compound semiconductors are widely used in optoelectronic devices e.g. infrared and visible light emitting diodes (LEDs), optical fiber communications and high efficiency solar cells [1, 2], precisely because of the stronger coupling between the semiconducting and optical properties in these materials.

As a further example, transistors based on semiconducting Si are used for data processing, while data storage is accomplished using ferromagnetic hard drives with the magnetic information being extracted using magnetic multilayers GMR (Giant Magneto-resistance) structures as read heads, allowing their large storage capacity [3]. Multifunctional materials having both semiconducting and ferromagnetic properties simultaneously, can potentially bridge the gap between data communication and data storage devices. These different materials properties can co-exist in undoped and transition metal doped compound semiconductors, called dilute magnetic semiconductors (DMS)[4, 5]. These materials open up the possibility of integrating the electron spin degree of freedom into the conventional charge-based electronic devices. This proposal to utilize both the electron spin and charge in electronic devices falls under the general title of “spin electronics” or “spintronics”. Spin dependent effects in these spintronic devices can arise from the interaction of the spin of the charge carriers with the magnetic properties of the materials. This is expected to lead to the development of next generation devices utilizing spin degree of freedom together with conventional microelectronics with a possibility of increased data processing speed, lower power consumption, non-volatility and increased integration densities [6]. One specific requirement for realizing spintronic devices is the efficient injection of spin polarized carriers into the semiconductors. Dilute magnetic semiconductors may provide much better spin injection than ferromagnetic metallic electrodes, since the impedance mismatch due to different electronic structure of magnetic and semiconductor materials significantly hinder the spin injection process. Multi-
functional spintronic materials having, for example, a strong coupling between the electron spin and the optical response, may offer other potential applications including quantum bits for quantum teleportation, quantum computation and communication, modulators, high frequency operating optical switches etc [6, 7].

The recently revived interest in a different class of multifunctional materials, in which two or more ferroic properties, being ferro or antiferroelectricity, ferro or antiferromagnetism and ferro or antiferroelasticity coexist in what are known as multiferroic materials is driven both by the potential applications of these systems as well as a desire to more deeply understand the physics underlying this behavior. Among these multiferroic materials, those displaying anti/ferromagnetic and anti/ferroelectric properties are known as magnetoelectric multiferroics. Magnetoelectric multiferroics provide an important advantage in designing new devices, due to the control of magnetic order using electric field. This may lead to the development of a new class of spin based electronics, magnetic sensors, transducers, and attenuators [8]. These technological benefits have made magnetoelectric multiferroics a very active area of research and has spurred the search and design of new multiferroic materials. One particular obstacle to the development of these materials is that the coexistence of ferromagnetic and ferroelectric properties is normally contra-indicated [9, 10]. Further studies are required to understand the microscopic mechanism producing this coexistence and coupling between typically mutually exclusive ferroic order parameters.

To harvest the widespread technological application of these multifunctional materials, it is important to understand the fundamental properties of these materials in both bulk and thin film geometry. While most devices will likely incorporate thin films of these materials, studies on bulk systems can often provide a more detailed understanding of the physics underlying this novel behavior. In my thesis, I will present the results of my experimental investigations on the optical and electronic properties of thin film group III-nitride and oxide based compound semiconductors together with my studies on room temperature
ferromagnetism and spin polarization in undoped and transition metal doped InN compound semiconductors. I will also present my work on the synthesis and magnetic, optical, thermal, dielectric, and magnetodielectric studies on the properties of bulk and thin films magnetoelectric multiferroics, YMnO$_3$, Ni$_3$V$_2$O$_8$, FeVO$_4$ compounds in order to understand the microscopic origin of magnetoelectric behaviour and explore the cross control between anti/ferromagnetic and ferroelectric properties.

### 1.2 COMPOUND SEMICONDUCTORS

Electronic materials can be generally classified as conductors, semiconductors, or insulators according to their electrical resistivities. The resistivities of good conductors and insulators are of the order of $10^{-8}$ or less and Ohm-cm, $10^8$ Ohm-cm or more respectively, whereas that for semiconductors this falls in the range of $10^{-4} - 10^6$ Ohm-cm at room temperature [11, 12]. Most semiconductors are either elements from group IV or are a combination of elements in groups equidistant from group IV on each side in the periodic table. A semiconductor periodic table is shown in Table 1.

Thus semiconductors can be elemental, e.g. silicon (Si), germanium (Ge) and can also be compounds, consisting of a combination of group III and group V elements or group II and group VI elements or group IV and group IV elements. These are known as group III-V, group II-VI or group IV-IV compound semiconductors respectively. The simple combination of elements from these pairs results in binary compound semiconductors e.g. Ga$^{IV}$N$^V$, 

<table>
<thead>
<tr>
<th>IIB</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
</tr>
<tr>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
</tr>
</tbody>
</table>

Table 1.1: Semiconductor periodic table
there are also compound semiconductors involving two or more elements from the same group. Such alloying can result in the formation of ternary compounds, e.g. Ga\textsuperscript{III}In\textsuperscript{III}N\textsuperscript{V}, Hg\textsuperscript{II}Cd\textsuperscript{II}Te\textsuperscript{VI}; quaternary compounds, e.g. Ga\textsuperscript{II}Al\textsuperscript{II}In\textsuperscript{II}N\textsuperscript{V} or even higher order compound semiconductors [13].

1.2.1 NITRIDE COMPOUND SEMICONDUCTORS

Alloying a group III element with nitrogen (group V) produces a nitride compound semiconductor, e.g. GaN, InN, AlN binary alloys, InGaN, InAlN ternary alloys, or InGaAlN quaternary alloys. Recent developments in nitride semiconductors over other group III-V semiconductors open up the possibility of full spectrum solid state light sources, from infrared (IR) to the ultra violet (UV). Among these nitride semiconductors GaN, having a wide bandgap $E_g \sim 3.4$ eV, is one of the most studied semiconductor. This material has led to the development of various lasing devices e.g. blue, green, and white light emitting diodes (LED) and laser diodes (LDs) [14]. A number of unanswered questions remain concerning the properties of the binary compound InN, in particular the value of the bandgap $E_g$. The previously accepted bandgap value of InN was $\sim 1.8$eV [15], is now attributed to various donor defects in the system [16]. The recent improvements in the quality of InN samples suggests that the correct bandgap is $\sim 0.7$-$0.9$eV [17, 18], which is in agreement with the density functional theoretical (DFT) calculated band gap values in the local density approximation (LDA) [19]. This new bandgap value of InN allows the In$_{1-x}$Ga$_x$N solid solution series to have bandgap values ranging from the infrared 0.7eV (x=0) to the ultraviolet 3.4eV (x=1), which would cover the entire solar spectrum [20]. This wide bandgap range for In$_{1-x}$Ga$_x$N system provides the possibility to fabricate multi-junction solar cells covering the entire solar energy spectrum [21]. Another advantage of nitride compound semiconductors over other semiconductors is that these are, in general, high band gap materials (except InN), which may be useful for high-power electronic devices. Additionally In$_{1-x}$Ga$_x$N exhibits superior high en-
ergy radiation resistance and chemical resistance, which make this system advantageous for space applications [22].

The excellent semiconductor electronic properties of these nitride semiconductors such as high saturation velocity and mobility have attracted attention towards spintronics applications using magnetic dopants in the host nitride semiconductor matrix. Theoretical studies by Dietl et al. [23] have shown that dilutely transition metal doped nitride semiconductors may be a possible candidate for room temperature ferromagnetic semiconductors. These room temperature dilute magnetic semiconductors (DMSs) may lead to the development of new devices utilizing the additional spin degree of freedom together with conventional electronic charge, leading to the spintronic devices [3].

1.2.2 OXIDE COMPOUND SEMICONDUCTORS

In general, oxide semiconductors are from group II and group III elements alloyed with Oxygen (group VI) and are typically wide bandgap semiconductors. The large bandgap makes these compounds transparent to visible light, leading to the appellation of transparent oxide (TO) semiconductors. Some common group II oxide compound semiconductors are Mg$^{II}\text{O}^{VI}$, Zn$^{II}\text{O}^{VI}$, Cd$^{II}\text{O}^{VI}$ while the group III binary compounds include Al$^{III}\text{O}^{VI}$, Ga$^{III}\text{O}^{VI}$ and In$^{III}\text{O}^{VI}$. These intrinsic binary oxide compound semiconductors are in general highly resistive and have moderate to high dielectric constants, which make these oxide materials as a good candidate for gate dielectric materials [24]. Their resistivity can be tailored by appropriate dopants in the host matrix and can be converted into highly conducting transparent materials. This led to the development of transparent conducting oxide (TCO) semiconductors, which are useful for many electronic applications [24]. Some well known examples of TCOs include aluminium doped ZnO ($\text{Zn}_1-x\text{Al}_x\text{O}$) and tin doped In$\text{O}_3$ ($\text{In}_{2(1-x)}\text{Sn}_x\text{O}_3$).

The recent surge of interest in these oxides is due, in part, to the possibility of intrinsic
ferromagnetism in undoped and transition element doped oxide compound semiconductors [25, 26]. A theoretical study by Dietl et al [27] has shown that ZnO based systems may be good candidates for high temperature ferromagnetic semiconductors. Recently Raghava et al [28] have shown that undoped In$_2$O$_3$ is ferromagnetic above room temperature due to the incorporation of oxygen vacancies. This system shows $\sim$55\% spin polarization at low temperatures, which makes it a possible transparent spin electronic material for spintronics applications. Beyond these interesting physical properties, the origin of ferromagnetism in undoped and transition elements doped oxide and non-oxide semiconductor is still vigorously debated. Further detailed studies are needed to address such issues in these systems.

### 1.3 MULTIFUNCTIONAL OXIDE MULTIFERROICS

Materials exhibiting more than one ferroic order, such as anti/ferroelectricity, anti/ferromagnetism, ferroelasticity, and ferrotoroidicity, have received renewed interest due to their potential technological applications and interesting physical phenomenon [8, 29]. These multifunctional materials are called multiferroics. Magnetoelectric multiferroics exhibit the coexistence of coupled long range (ferro)antiferromagnetic and ferroelectric orders in one material [8]. The coupling between different ferroic orders enables one to manipulate the ferroelectric order by applying a magnetic field and, conversely, the magnetic ordering by applying an electric field. Thus, the switching of the spontaneous polarization and spontaneous magnetization can be controlled by applying magnetic and electric fields respectively. This cross-control provides additional functionality, which is crucial for many magnetoelectronic devices.
Chapter 2

MULTIFUNCTIONAL MATERIALS
-THEORETICAL AND
EXPERIMENTAL REVIEW
(DIFFICULTIES AND
CHALLENGES)

2.1 SEMICONDUCTORS AND THEIR CLASSIFICATIONS

Semiconductors are defined as materials with an electrical resistivity (or conductivity) lying in the range of $10^{-2}(10^{2}) - 10^{8}(10^{-8})$ Ohm.cm (mho.cm$^{-1}$). Alternatively, materials with an energy gap ($E_g$) between a few meV (below which thermal excitations would produce large occupation of conducting states) and $\sim 4$ eV can also be considered semiconductors. Materials with a partially filled conduction band having a finite electronic density of states
Figure 2.1: Schematic energy band diagram for insulators, semiconductors and metals [30] at the Fermi level or a very small overlap between conduction band and valence band with a negligible density of states at the Fermi level are metals or semimetals respectively, while those with an energy gap greater than 4 eV are insulators. These boundaries differentiating metals, semiconductors and insulators are not sharply defined and there are exceptions to these general rules. For example, aluminum nitride (AlN) and diamond are considered to be wide band gap semiconductors with $E_g \sim 6.2$ eV and 6eV respectively, while GaAs is classified as semi-insulating with $E_g \sim 1.5$ eV. The schematic energy band pictures of insulators, metals, and semiconductors is shown in Fig 2.1.

The development of energy bands from localized orbits for silicon is explained in detail in Appendix A(1). This energy band model classifies semiconductors into two types-direct bandgap semiconductors and indirect bandgap semiconductors. Semiconductors having the same value $k_{min}$ of the wave vector $k$ (in general $k =0$) for the lowest energy state in the conduction band and the highest energy state in the valence band $k_{max}$ i.e. the minima of
Figure 2.2: Schematic E-k diagram for (a) direct bandgap semiconductor and (b) indirect bandgap semiconductors

Conduction band and maxima of valence band lie at the same \( k \), are called direct bandgap semiconductors. These include GaN, InN, and GaAs among others. A schematic \( E-k \) energy band diagram for direct bandgap semiconductors is shown in Fig.2.2(a). Semiconductors for which wave vector minimum \( k_{\text{min}} \) of the conduction band is different from the wave vector maximum \( k_{\text{max}} \) of the valence band, that is the minima of the conduction band and maxima of the valence band do not have the same \( k \), are indirect semiconductors, and include Si and Ge. The schematic \( E-k \) energy band diagram for indirect semiconductor is shown in Fig 2.2(b). Electrical conduction in a pure semiconductor, whether direct or indirect, is due to thermally generated intrinsic charge carriers. These are in generally very small in numbers, for example only \( \sim 10^9 \) electrons/cm\(^3\) in silicon, and are only available in the conduction band at or above room temperature [13]. At very low temperatures, there will be no electrons in the conduction band of intrinsic semiconductors. This explains why an intrinsic semiconductor behaves as a perfect insulator close to absolute zero. The property that makes semiconductors relevant for many device applications is that their electrical conductivity can tuned by adding small concentrations of impurities. Samples where the
electrical properties are tuned by additional dopants are known as extrinsic semiconductors. The type of dopant used controls the conduction mechanism in these materials. If the dopant provides additional electrons to the host semiconductor, the system is called a \( n \)-type semiconductor, whereas if the dopants provides additional holes, the system is called a \( p \)-type semiconductor. In general, a very small amount, less than one defect atom per million host atoms is sufficient to change the semiconductor properties for device applications. These defects can be beneficial or detrimental to the properties of the semiconductor.

In an intrinsic semiconductors, the charge carriers are thermally activated and usually the electrons and holes are present in equal numbers. The electron and hole carrier concentrations in an intrinsic semiconductor are given by:

\[
n = \int_{E_c}^{E_{top}} g_c(E) \times f(E) \, dE
\]

(2.1)

and

\[
p = \int_{E_{bottom}}^{E_v} g_v(E) \times (1 - f(E)) \, dE
\]

(2.2)

where \( g_v(E)dE, g_c(E)dE \) are the number of valence and conduction band states per cm\(^3\) in the energy range \( E \) and \( E + dE \) and \( f(E) \) and \( (1 - f(E)) \) are the probabilities that an available state at an energy \( E \) will be occupied by an electron or a hole. The integration in Eq (2.1) is taken from the bottom of the conduction band \( E_c \) to the top of the band while in Eq (2.2) the integral is taken from the bottom of the valence band to the top \( E_v \).

After simplifying the limits in the integral for Eqs (2.1) and (2.2) and using the Fermi-Dirac function \( f(E) \) for the electron (or hole) distribution, these equations reduces to:

\[
n = N_c \frac{2}{\sqrt{\pi}} F_\frac{1}{2}(\eta_c)
\]

(2.3)

and

\[
p = N_v \frac{2}{\sqrt{\pi}} F_\frac{1}{2}(\eta_v)
\]

(2.4)
where \( N_c = 2\left(\frac{m^*kT}{2\pi\hbar^2}\right)^{3/2} \) and \( N_v = 2\left(\frac{m^*kT}{2\pi\hbar^2}\right)^{3/2} \) are the effective density of conduction and valence band states and \( F_{\frac{1}{2}}(\eta) \) is the Fermi-Dirac integral of order 1/2 and \( \eta_c = \frac{(E_F - E_C)}{kT} \); \( \eta_v = \frac{(E_v - E_F)}{kT} \) where \( E_F \) is the Fermi energy of the system. If the Fermi energy \( E_F \) lies in the range \( E_v + 3kT \leq E_F \leq E_c - 3kT \), then the expression for \( n \) and \( p \) simplifies to:

\[
n = N_c e^{\frac{(E_F - E_C)}{kT}} \quad \text{and} \quad p = N_v e^{\frac{(E_v - E_F)}{kT}}
\]

These expressions for \( n \) and \( p \) are valid if \( E_F \) lies in the conduction or valence band and no closer than 3kT to either band edge. When \( E_F \) is confined in this range, the semiconductor is called non-degenerate and whenever \( E_F \) lies within 3kT of either band edge the semiconductor is called degenerate. The schematic difference between non-degenerate and degenerate semiconductor is shown in Fig 2.3.

So far we have considered undoped intrinsic semiconductors, where number of electrons is the same as number of holes and their density can be written as:
\[ n = p = n_i = (N_c N_v) \frac{1}{2} e^{-E_g/2kT} \] (2.6)

where \( E_g = E_c - E_v \) is the bandgap. The concentration of charge carriers can be changed by introducing dopants leading to extrinsic semiconductors. The charges can be electrons, holes, positively charged ionized donors (which donate electrons to the conduction band), and negatively charged ionized acceptors (which donate holes to the valence band). Under equilibrium conditions the total charge due to extrinsic impurities and charge carriers is zero, that is, the system contains no net effective charge. This is known as the ”charge neutrality condition”, even though charged entities are present everywhere in the semiconductor. Mathematically charge neutrality condition is expressed as:

\[ p - n + N_D^+ - N_A^- = 0 \] (2.7)

where \( p, n, N_D^+ \) and \( N_A^- \) are the number of holes, electrons, positively charged donors and negatively charged acceptors per unit volume. Using the charge neutrality condition and the relation \( n.p = n_i^2 \), the carrier concentrations \( n \) and \( p \) under non degenerate conditions for an extrinsic semiconductor are given by:

\[ n = \frac{N_D - N_A}{2} + \left[ \left( \frac{(N_D - N_A)}{2} \right)^2 + n_i^2 \right]^\frac{1}{2} \] (2.8)

and

\[ p = \frac{n_i^2}{n} = \frac{N_A - N_D}{2} + \left[ \left( \frac{(N_A - N_D)}{2} \right)^2 + n_i^2 \right]^\frac{1}{2} \] (2.9)

These equations provide the electron and hole carrier densities in an extrinsic semiconductor. For intrinsic semiconductors \( N_D = 0 = N_A \); substituting these into the equations above one find \( n = n_i = p \) under equilibrium conditions. For \( n \)-type extrinsic semiconductors, where the excess electron charge carriers are provided by donor impurities,
\[ N_D - N_A \simeq N_D \gg n_i. \] Thus for \( n \)-type extrinsic semiconductors the previous equations for electron and hole concentrations become:

\[
n \simeq N_D & p \simeq \frac{n_i^2}{N_D} \tag{2.10}
\]

and similarly for \( p \)-type extrinsic semiconductors, where the excess charge carriers are holes and are provided by acceptor impurities \( N_A - N_D \simeq N_A \gg n_i \). In these materials the hole and electron carrier concentrations are given by:

\[
p \simeq N_A & n \simeq \frac{n_i^2}{N_A} \tag{2.11}
\]

This flexibility in tuning the carrier concentrations and type of charge carriers in semiconductors make them useful for numerous microelectronic applications. In many cases, it is difficult to avoid introducing various defects during and subsequent to the fabrication process leading to highly degenerate systems. These accidental charge carriers cloak the intrinsic materials properties of the semiconductor and may make them unsuitable for the desired application. We will discuss the effect/influence of numerous defects introduced during and after the growth process for highly degenerate \( n \)-type InN and \( \text{In}_2\text{O}_3 \) compound semiconductors and will explore some possible application for these highly degenerate semiconductors.

### 2.2 MULTIFUNCTIONAL MAGNETIC SEMICONDUCTORS

Magnetic semiconductors exhibit both magnetic and semiconducting properties. One general approach to make a magnetic semiconductor is to replace a small fraction of cations in the non-magnetic parent semiconductor by magnetic ions, which produces a dilute magnetic
Figure 2.4: A schematic representation of (a) a non-magnetic and (b) a dilute magnetic semiconductor (DMS). A schematic representation of this process is shown in Fig. 2.4.

The magnetic interaction among local spins on these magnetic ions together with the charge carriers gives rise to ferromagnetism in these systems. These DMSs are promising materials for spintronic device applications provided their Curie temperature $T_c$ is above room temperature. A number of DMS systems have been identified and are widely studied including Mn doped InAs [32] and GaAs [33], which have Curie temperatures of 35 K and 170 K respectively. This low magnetic transition temperature makes these materials impractical for device applications but these materials have helped to guide the search for new DMS materials with ferromagnetic order above room temperature.

Theoretical work by Dietl et al showed that Mn doped GaN and ZnO could be ferromagnetic above room temperature, given certain materials assumptions [27]. Ab initio electronic structure calculations by Sato et al have also predicted ferromagnetic ordering in transition metal doped ZnO [34, 35]. These theoretical results propelled additional research into DMS materials, leading to the discovery of numerous transition metal doped semiconductors with ferromagnetism above room temperature. Extensive work on various transition metal doped oxides including TiO$_2$, ZnO, In$_2$O$_3$, SnO$_2$ has been carried out to search for ferromagnetism, which has been observed at or above room temperature in many of these systems [36]. Re-
markably, even undoped In$_2$O$_3$ has shown high temperature ferromagnetism together with 55% spin polarization at low temperatures [28]. Whereas these DMSO systems have opened the possibility of developing room temperature spintronic devices, the origin of this ferromagnetism remains highly controversial due to the lack of reproducibility and large variations in the measured magnetic properties in these materials [37]. The main puzzle is whether the magnetism in these systems is due to the uniformly distributed transition metal ions in the host matrix or due to the presence of secondary phases, including magnetic impurity phase clusters. For possible technological applications of DMSs, it is important to understand the origin of ferromagnetism in these systems. A number of different mechanism have been proposed to explain the onset of ferromagnetism in DMSs. The most commonly used models to explain the development of ferromagnetism in these systems are explained briefly in the following section.

### 2.3 ORIGIN OF MAGNETISM AND SPIN POLARIZATION IN DILUTE MAGNETIC SEMICONDUCTORS

The DMSs can be considered as magnetically inactive host semiconductor with localized spins, arising from dopants or defects, as shown in Fig 2.4. The host semiconductor may also be doped with either electrons or holes acting as mobile charge carriers, which can promote carrier mediated magnetism in these systems [27, 34]. The magnetic interactions in these systems are usually determined by the $sp - d$ electronic exchange, where the s and p orbitals belong to the host and carrier donors and d orbitals to the transition metal ions. Electronic exchange interactions through carriers in the conduction or valence bands in the system may give rise to the magnetic ordering.
2.3.1 ZENER MODEL

This model attributes the magnetism in dilute magnetic alloy systems to effects arising from the exchange interaction between localized spins of transition metal ions and charge carriers in the system [38, 39, 40]. This model suggests that the direct superexchange [41] interaction between the half filled d-orbitals of the localized electrons electrons on the transition metal cations and the completely filled p-orbitals of the anion is antiferromagnetic. The d-orbital electrons from adjacent transition metal atoms overlap the same p-orbitals, so their spins will be antiparallel by the Pauli exclusion principle. This will give rise to AFM coupling between nearest neighbour transition metal cations mediated by a shared anion, as explained in Fig 2.5(a).

If the interaction between localized d-orbital electrons on the transition metal cations through the delocalized charge carriers in the system is indirect superexchange, the transition metal cations d-orbital electrons will align ferromagnetically, as shown in Fig 2.5(b). Thus, the Zener model suggests that ferromagnetic ordering in dilute magnetic alloys develops only when the indirect exchange interaction is much larger than direct superexchange. According to this model, the spin coupling energy in dilute magnetic alloys consists of three main terms:
(1) the direct exchange between $d$-orbital electrons, (2) the exchange between the $d$-orbital electrons and the conduction electrons and (3) the Fermi kinetic energy of the conduction electrons. When the spin distribution at Fermi level is symmetric, that is the density of states for spin up and spin down electrons are same, the kinetic energy will tend to zero.

The spin energy $E_{\text{spin}}$ after combining all three types of spin coupling is given by:

$$E_{\text{spin}} = \frac{1}{2} \alpha S_d^2 - \beta S_d S_c + \frac{1}{2} \gamma S_c^2$$  \hspace{1cm} (2.12)

where $S_c$ and $S_d$ are the spin polarizations of the conduction electrons and $d$-orbital electrons respectively, and $\alpha$, $\beta$ and $\gamma$ are the respective coefficients. At equilibrium $E_{\text{spin}}$ will be at a minimum and the spin polarization for conduction electron can be expressed in terms of the spin polarization of $d$-orbitals as:

$$S_c = \frac{\beta}{\gamma} S_d$$  \hspace{1cm} (2.13)

Substituting this value of $S_c$ in Eq (2.12), the $E_{\text{min}}$ is given as

$$E_{\text{spin}} = \frac{1}{2} (\alpha - \frac{\beta^2}{\gamma}) S_d^2$$  \hspace{1cm} (2.14)

The type of magnetic behaviour can be determined by only the relative magnitude of the $\beta^2$ and $\alpha \gamma$ terms. When $\beta^2 > \alpha \gamma$, the system will order ferromagnetically and $E_{\text{spin}}$ will be negative and if $\beta^2 < \alpha \gamma$, the system will order antiferromagnetically and $E_{\text{spin}}$ will be positive.

### 2.3.2 RUDDERMAN-KITTEL-KASUYA-YOSIDA (RKKY) MODEL

The RKKY model describes the magnetic interaction between a single localized magnetic ion and delocalized free electrons. The conduction electrons near the localized
magnetic ion become magnetized, or spin polarized, following an oscillatory wave, whose amplitude decays with increasing distance. The nature of this polarization wave depends on the RKKY exchange parameter $J(r)$, which is given as [42]

$$J(r) = \frac{m^* k_F^4}{\hbar^2} F(2k_F r)$$  \hspace{1cm} (2.15)

where $m^*$ is the electron effective mass and $k_F(=\frac{3}{2}\pi^2 n_e)$ is Fermi wave vector, $n_e$ is the conduction electron density and $F$ is the function given as:

$$F(2k_F r) = \frac{2k_F r \cos(2k_F r) - \sin(2k_F r)}{(2k_F r)^4}$$  \hspace{1cm} (2.16)

The variation of the RKKY exchange parameter $J(r)$ with respect to the distance from the magnetic ion is shown in Fig 2.6.

This oscillation mediates either FM or AFM magnetic exchange coupling depending on the separation between adjacent magnetic ions. The magnetic coupling will be ferromagnetic for higher magnetic impurity concentrations and lower electron densities, satisfying the condition $2k_F r < 4.5$. The magnetization and Curie temperature scale with the magnetic impurity concentration in this regime. On the other hand, a lower concentration of

![Figure 2.6: RKKY exchange parameter J(r) oscillations as a function of r, the distance from a magnetic ion](image)

- RKKY exchange parameter $J(r)$ oscillations as a function of $r$, the distance from a magnetic ion.
magnetic impurities and higher conduction electron densities, the competing FM and AFM interactions in conjunction with disorder, can give rise to a spin glass state [43]. This model is appropriate for systems with high conduction electron densities such as rare earth metals, where the 5\textit{d} and 6\textit{s} electrons serve as the conduction electrons, and mediate ferromagnetic interactions between the localized 5\textit{d} magnetic ions of the system.

### 2.3.3 MEAN FIELD ZENER MODEL

A modified Zener model was proposed by Dietl et al [27] to understand the ferromagnetism in \textit{p}-type DMSs. This relies on the Zener indirect superexchange interaction among the local moment dopants mediated by free holes, not by free conduction electrons. The mean field Zener model considers the valence-band structure of the ferromagnetic semiconductors, unlike the RKKY model where the conduction band structure was considered. Dietl et al have predicted the observed magnetic properties for hole mediated GaMnAs and ZnMnTe systems using the mean field Zener model. Additionally using this model, they have predicted the Mn doped \textit{p}-type GaN and ZnO systems will exhibit ferromagnetism at or above room temperature, as shown in Fig 2.7. This model suggests that hole mediated exchange is an important ingredient for producing ferromagnetism. Additionally Sato et al [34] have predicted that high temperature ferromagnetism can also be stabilized in \textit{n}-type ZnO system as well.

### 2.3.4 ZENER DOUBLE EXCHANGE MODEL

Ab initio electronic structure calculations for Fe, Co and Ni doped ZnO by Sato et al [34], indicate that \textit{n}-type doping in ZnO can increase the Curie temperature above room temperature, with the double exchange interaction between two neighbouring transition metal ions giving rise to ferromagnetism. This double exchange interaction mechanism was first proposed by Zener to explain ferromagnetism in the manganites [39]. This interaction
Figure 2.7: Curie temperature for different p-type semiconductor containing 5% Mn [23]
takes place by the hopping of electrons between two neighbouring transition metal ions.
The $3d$ energy levels of transition metal splits into doublet $e_g$ and triplet $t_{2g}$ energy levels
depending on the octahedral or tetrahedral geometry and crystal field energy. The spin up
and spin down states are non-degenerate because of the exchange splitting. For example
spin up Co $3d$ states are lower in energy than Co $3d$ spin down states in Co doped ZnO with
the Co $3d$ spin down states lying below the conduction band. These states are also strongly
hybridized with oxygen $2p$ states so if the neighbouring Co spins are aligned parallel, the
electrons in the partially filled $3d$-orbitals of the Co ions are allowed to hop from one Co ion
to the other and thus stabilizing the ferromagnetic ground state, as shown in Fig 2.8.

### 2.3.5 BOUND MAGNETIC POLARON (BMP) MODEL

The ferromagnetism in DMSs, especially in transition metal doped or undoped oxide
semiconductors, has also been explained by the bound magnetic polaron (BMP) model, aris-
Figure 2.8: Schematic representation of the double exchange interaction between adjacent Co$^{2+}$ ions leading to ferromagnetic coupling

...ing from the exchange interaction between large collections of spins of transition metal ions mediated by charge carriers, electrons or holes, localized near the TM ions. The overlap of neighbouring bound magnetic polarons results in long range ferromagnetic ordering above the percolation threshold. The temperature for magnetic ordering produced by this mechanism depends on the nature of interactions between TM atomic spins and the charge carriers. Durst et al [44] have computed this exchange based on their polaron-pair model, as shown in Fig 2.9.

In this pair polaron model [44], all magnetic ions within a sphere of radius $R$ about a carrier interact with that carrier with the same exchange constant $K$. Thus a polaron in this model is composed of a single charge carrier and the magnetic ions within a radius $R$ of the impurity site to which the carrier is bound. The interaction between two BMPs is considered through an interstitial region between them in which TM ions interact significantly with both carriers, with an exchange constant $K'$. This interstitial region is required for the indirect ferromagnetic carrier-ion-carrier interaction to be significant. Considering these interactions,
the Hamiltonian can be written as:

$$H_m = K[(\vec{s}_1 . \vec{S}_1) + (\vec{s}_2 . \vec{S}_2)] + K'(\vec{s}_1 + \vec{s}_2).\vec{S}_3 + J\vec{s}_1 . \vec{s}_2$$  \hspace{1cm} (2.17)$$

where $K$ is the intra-polaron ion-carrier exchange constant, $K'$ is the interstitial ion-carrier exchange constant, $J$ is the direct carrier-carrier exchange constant as explained in the Fig 2.9, $\vec{s}_1$ and $\vec{s}_2$ are the carrier spins, $\vec{S}_1$ and $\vec{S}_2$ are the net polaron spins and $\vec{S}_3$ is the collective spin of the interstitial region. The bi-polaron model, shown in Fig 2.9, illustrates the competition between the direct AFM carrier-carrier interactions characterized by $J$ and the indirect FM carrier-ion-carrier interactions characterized by $K'$. In DMSs, the donor bands are relatively large and the $s – d$ interactions are not very strong. Therefore BMPs formed through $s – d$ exchange interactions can exhibit collective FM ordering only at low
temperatures. However, if more localized valence bands, such as formed from $p$ orbitals [NB or $s - p$ hybrid orbitals?] are involved in the formation of BMPs, the $p - d$ exchange interaction is strong enough to produce long range ordering even at higher temperatures.

Coey et al applied this model to dilute magnetic oxide semiconductors to explain the observed ferromagnetism in these systems. They suggested that the FM exchange coupling of transition metal ions in $n$-type dilute magnetic oxide semiconductors is mediated by shallow donor electrons trapped by the oxygen vacancies, which facilitate the formation of BMPs within their hydrogenic orbits. This is illustrated in Fig 2.10.

In general dilute magnetic oxide semiconductors can be chemically represented as $(A_{1-x}M_X)(O\square_{\delta n})$, where $A$ is a non-magnetic cation, $M$ is a transition metal cation, $O$ is the oxygen, $\square$ is a donor defect and $n = 1$ or 2. The electrons associated with defects will be confined in a hydrogenic orbital [45]. The $sd$ exchange energy $\delta E_{ex}$ between the hydrogenic
electron and transition metal cation is given by:

\[ \delta E_{ex} = -J_{sd} \vec{S} \cdot \vec{s} |\psi(r)|^2 \Omega \]  

(2.19)

where \( j_{sd} \) is the \( sd \) exchange parameter, \( \vec{S} \) is the effective spin of the transition metal ions in a volume \( \Omega = \frac{4}{3} \pi r_c^3 \), with radius \( r_c \) of the transition metal cation, \( \vec{s} \) is the donor electron spin and \( \psi(r) \) is the \( 1s \) orbital donor electron wave function. The increased electron density \( |\psi(r)|^2 \) will increase the exchange energy and therefore the Curie temperature. This relation is given by:

\[ T_c = S(S + 1) s^2 n x \delta J_{sd}^2 \frac{\omega_c^{2/3}}{k_B \epsilon_F} \]  

(2.20)

where \( s \) and \( S \) are the donor electron and transition metal impurity ions respectively, \( x \) is the transition metal ion concentration, \( \delta \) is the donor concentration, \( \omega_c \) is the cation volume fraction and \( \epsilon_F \) is the Fermi energy. This model suggests that if the transition metal impurity concentration \( x \) is greater than the percolation threshold, \( x_p \), then direct AFM ordering is more favourable. However, if the donor concentration \( \delta \) exceeds the polaron percolation threshold concentration \( \delta_p \), the indirect carrier mediated FM interactions will dominate.

### 2.3.6 \( d^0 \) MODEL-MAGNETISM IN SYSTEMS WITHOUT MAGNETIC IMPURITY DOPANTS

High temperature ferromagnetism developing in the absence of any magnetic ions has been observed in numerous material systems, including carbon or graphite [46, 47], hexaborides [48], HfO\(_2\) [49], oxide and nitride compound semiconductors [50, 43]. These systems exhibit diamagnetic behaviour when prepared as defect free stoichiometric samples, but can show high temperature ferromagnetism under non stoichiometric conditions. For example, oxygen deficient binary oxides such as HfO\(_2\) [49], TiO\(_2\) and In\(_2\)O\(_3\) [28] may show weak ferro-
magnetism above room temperatures. These systems, which formally lack any partially filled $d$ (transition (TM) metal ions) or $f$ (rare earth (RE) metal ions) orbital impurity atoms, to form local moments or create a narrow spin-split band in the host are called $d^0$ systems. The presence of lattice defects is a common feature in these $d^0$ systems, and these defects can form an impurity band inside the bandgap of the host system. If the density of states is sufficiently large, spontaneous spin splitting based on the Stoner criterion $D(E_F)I > 1$, where $D(E_F)$ is the density of states at the Fermi level and $I$ is the band exchange integral, may lead to the ferromagnetism in these system [51].

### 2.3.7 CHARGE TRANSFER FERROMAGNETISM-A MECHANISM FOR DEFECT-RIDDEN OXIDE SYSTEMS

Coey et al recently proposed a charge transfer mechanism for the observed high temperature ferromagnetism in doped oxides and other material systems [37]. The main components required for the mechanism are a defect mediated band near the Fermi level with a high density of states, an electron charge reservoir, and an effective exchange integral $I$ associated with the defect states. In this model, if the effective Stoner exchange integral $I$ is large enough, the energy gain from exchange splitting the defect band will compensate for the energy cost of transferring electrons from the charge reservoir [52], in addition to the standard kinetic energy cost of the band splitting. This model proposes that the magnetization will be non-uniform and suggests that regions containing defects become ferromagnetic in contrast to the standard Stoner model, which predicts only a uniform magnetization. The schematic mechanisms for charge transfer ferromagnetism is shown in Fig 2.11.

Electrons are transferred from the charge reservoir to the defect band or vice versa, which will thus increase the density of states $D(E_F)$ at the Fermi level in the defect band until the Stoner criterion $D(E_F)I > 1$ is satisfied resulting into ferromagnetic ordering in these defect-rich regions. This would suggest that only a small volume of the sample is actively
Figure 2.11: Schematic representation of charge transfer magnetism; electron transfer between the charge reservoir and the defect band can satisfy the Stoner criterion leading to ferromagnetic splitting [37]

involved in the observed ferromagnetism, which could potentially be tested experimentally.

We have studied the magnetism in undoped and Cr doped InN n-type highly degenerate systems. We find that these systems exhibit ferromagnetism above room temperature and having a spin polarization of 40% at low temperatures. We will discuss the role of defects producing the highly degenerate nature and their correlation with the magnetic properties. Additionally we will also discuss the importance of oxygen vacancies and indium interestials on the origin of high temperature ferromagnetism in In$_2$O$_3$.

### 2.4 MULTIFUNCTIONAL MULTIFERROICS

The integration of new functionalities in a material generates additional degrees of freedom to interact with various physical properties. For example, the spin of electrons in DMS provide an additional degree of freedom couple to electronic charge. Multiferroics represent another such class of multifunctional systems, which show at least two ferroic orders simultaneously in a single phase material [53]. These ferroic orders are anti/ferromagnetism, anti/ferroelectricity, ferroelasticity, and ferrotoroidicity. The simultaneous co-existence of
both magnetic and ferroelectric order is often associated with magnetoelectric (ME) coupling, which can cross control of magnetic and electric properties in these materials. Typically, magnetoelectric coupling produces a polarization in an applied magnetic field, as a linear effect, or by applying both electric and magnetic fields simultaneously, as an non-linear effect [54, 55, 56]. This also includes the converse coupling, the induction of a magnetization by an electric field.

The phenomenon of intrinsic ME effect was predicted by P. Curie in 1894 based on crystal symmetry arguments [57]. I. E. Dzyaloshinskii [58] explained the ME effect in antiferromagnetic Cr$_2$O$_3$ by explaining the violation of time-reversal symmetry, which was confirmed experimentally by Astrov showing electric field induced magnetization [59] and by Rado et al showing magnetic field induced polarization [60]. After these experiments various linear magnetoelectric compounds were discovered. A comprehensive list of linear magnetoelectric compounds was compiled by H. Schmid [61]. These linear magnetoelectric materials, which are generally referred to simply as magnetoelectrics, often show long range magnetic ordering but do not typically develop any spontaneous polarization. Yet an electric polarization can be induced by applying a magnetic field. In contrast, multiferroics exhibit both spontaneous magnetic order and polarization in a single phase material even in the absence of applied electric or magnetic fields. Linear magnetoelectric materials can be explored by considering magnetic point group symmetry [61, 62]. In a single-phase crystals, the ME effect can be described in Landau theory using the expansion of the total free energy $F$ in terms of the applied magnetic field $H$ and electric field $E$, i.e.

$$F(E,H) = F_0 - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \chi_0 \chi_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_j E_i E_k + ... \quad (2.21)$$

where $\epsilon_0$ and $\chi_0$ are the free space permittivity and permeability, $\epsilon_{ij}$ and $\epsilon_{ij}$ are the relative permittivity and permeability, $\alpha_{ij}$ is the linear magnetoelectric tensor and $\beta_{ijk}$ and
\( \gamma_{ijk} \) are higher order magnetoelectric tensors. The polarization and magnetization can be obtained by differentiating above equation with respect to electric field and magnetic field respectively and are given by:

\[
P_i = -\frac{\partial F}{\partial E_i} = \frac{1}{2} \epsilon_{0} \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + ..
\]

\((2.22)\)

and

\[
M_j = -\frac{\partial F}{\partial H_j} = \frac{1}{2} \chi_{0} \chi_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + ..
\]

\((2.23)\)

Thus, a necessary condition for all linear ME material is that they must contain the linear term \( \alpha_{ij} E_i H_j \), where the tensor \( \alpha_{ij} \) corresponds to the induced polarization or magnetization by an applied magnetic or electric field respectively. This is not the necessary condition for being a multiferroic. The classic example is \( \text{Cr}_2\text{O}_3 \), which is a linear ME material but not a multiferroic as it is not an intrinsic ferroelectric. Thus all linear ME materials are not multiferroics and vice-versa; all multiferroics are not linear ME materials. For example, \( \text{YMnO}_3 \), which is a multiferroic (exhibits antiferromagnetic and ferroelectric ferroic orders simultaneously) but not a ME as symmetry of this compound does not allow linear ME effect \cite{63}. The detailed taxonomy of magnetoelectric and multiferroic materials is given by Eerenstein et al \cite{53}. The schematic relationship between multiferroic and magnetoelectric materials motivated by Eerenstein et al \cite{53} and D. Khomskii \cite{64} is shown in Fig. 2.12.

There are materials which are neither multiferroics nor linear ME, including \( \text{SeCuO}_3 \), \( \text{TeCuO}_3 \). These systems show dielectric anomalies at magnetic ordering temperature associated with higher order magnetoelectric coupling. Lawes et al observed a change in the dielectric constant by applying magnetic field, coupling between dielectric constant and magnetization \cite{65, 66}. This is marked in Fig 2.12 as a region without spontaneous polarization.

The linear magnetoelectric coefficient \( \alpha_{ij} \) represents the interaction between magnetic and ferroelectric degrees of freedom and is limited by the magnetic and electric susceptibilities of
Figure 2.12: Schematic representation of magnetic, ferroelectric, linear magnetoelectric, magneto-dielectric, and multiferroic systems
the materials [67]. This is always less than the geometric mean of the dielectric permittivity $\epsilon_{ij}$ and magnetic permittivity $\mu_{ij}$, as expressed by the following equation:

$$\alpha_{ij} < (\epsilon_{ii}\mu_{jj})^{1/2}$$ (2.24)

This inequality is an important constraint ensuring that the system is thermodynamically stable and also suggests that large permeability and permittivity values are essential to get a large magnetoelectric coupling. This limit is applicable to only linear ME materials so systems exhibiting higher order magnetoelectric effects may overcome this constraint [53].

### 2.5 TYPES OF MULTIFERROICS AND MICROSCOPIC ORIGIN OF MULTIFERROICITY

There was renewed interest in multiferroics after N. Hill papers [9, 10] highlighting that magnetism and ferroelectricity are contraindicated due to the chemical incompatibility of the physical origin of these ordering phenomena. In general magnetism arises from the presence of localized electrons in partially filled $d$ or $f$ shells of transition metal or rare earth ions. The exchange interaction between these local moments gives rise to magnetic ordering. Conversely cations having empty $d$-shells is required for ferroelectricity. For example, the ferroelectricity in BaTiO$_3$ is due (in large part) to the off-center displacement of Ti ion. This off-center displacement is only possible since the Ti$^{4+}$ ion has an empty $d$-shell. This competition is referred as $d^0$ vs $d^n$ problem [9, 10]. Therefore, different microscopic mechanisms are necessary to explain the onset of ferroelectricity in multiferroic materials. D. Khomskii subdivided multiferroics into type-I and type-II multiferroics, based on their magnetic and ferroelectric ordering temperatures [64]. Those multiferroics for which the ferroelectric and magnetic ordering temperatures are well separated are classified as type-I multiferroics. In these multiferroics the origins of magnetic and ferroelectric ordering are independent and
distinct. Two important and widely studied examples of type I multiferroics are BiFeO$_3$ [68] and YMnO$_3$ [69]. Multiferroics where the magnetic order produces the ferroelectricity, so that the ferroelectric ordering temperature coincides with a magnetic transition, are called type-II multiferroics. Some examples of type-II multiferroics are Ni$_3$V$_2$O$_8$ [70], FeVO$_4$ [71], TbMnO$_3$ [72].

2.6 MICROSCOPIC ORIGIN OF FERROELECTRICITY, MAGNETISM, AND MAGNETOELECTRIC COUPLING IN TYPE-I MULTIFERROICS

Type-I multiferroics are typically good ferroelectrics, having reasonably high values of the electric polarization and the ferroelectric and magnetic ordering temperature in these multiferroics are well separated. In this class of materials, the ferroelectric order arises from lattice or electronic considerations, without requiring the onset of magnetic order. These systems normally show ferroelectric transition temperatures above room temperature. However, the ME coupling between different order parameters is normally rather weak. Some of the possible mechanisms responsible for the onset of ferroelectricity, magnetism, and magnetoelectric coupling in these materials are explained in the following.

2.6.1 PARAMAGNETIC DOPING

Smolenskii et al suggested that doping paramagnetic cations into non-magnetic transition metal ions could lead to the simultaneous coexistence of ferroelectricity and magnetism [73]. In perovskite ABO$_3$, an empty $d$ shell ($d^0$) transition metal cation at the B site gives rise to ferroelectricity and a partial filled $d$ shell transition metal cation at B site is responsible
for ferromagnetism in the system. For example solid solutions of Pb(Mn$_{0.5}$Nb$_{0.5}$)O$_3$ and Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$, containing both an empty and partially filled transition metal cations, exhibit multiferroic properties [73]. These systems exhibit low magnetic ordering temperature due to the dilution of magnetic ions in the system.

\section*{2.6.2 Lone Pair Asymmetry}

In some of the perovskite ABO$_3$ systems, where B = Fe, Mn and Cr, stereochemical activity of lone pairs of cations at A site gives rise to ferroelectricity [9]. For example in BiFeO$_3$, BiMnO$_3$, BiCrO$_3$ and PbVO$_3$, energetically unstable 6s$^2$ lone pairs of electrons in Bi$^{3+}$ and Pb$^{2+}$ ions, which do not participate in chemical bonding, gives rise to displacements of the Bi or Pb cations from the center with respect to the neighbouring oxygen ions [10]. This results in ferroelectricity. Microscopically, the 6s$^2$ lone pair of electrons on cation A site may hybridize with an empty p orbital of oxygen leading to a localized charge lobe that causes a structural distortion and thus introducing ferroelectricity. This class of materials are known as 'proper ferroelectrics' because of their similarity with BaTiO$_3$, where ferroelectricity is mainly due to the structural instability with associated electronic pairing. The ME coupling between ferroelectric and magnetic ordering in these system is weak because the magnetism and ferroelectricity in such materials involves different cations.

\section*{2.6.3 Electronic Ferroelectricity (Charge Ordering)}

Ferroelectricity (electronic) in transition metal compounds with mixed valence transition metal ions is generally associated with charge ordering. If both sites and bonds are inequivalent after charge ordering, the broken symmetry allows ferroelectric order. Efremov et al have shown that certain divalent doped perovskites R$_{1-x}$Ca$_x$MnO$_3$, (R-rare earth metal), which exhibit an intermediate site-centered and bond centered charge ordering, show fer-
roelectricity [74]. Examples are Pr\textsubscript{1/2}Ca\textsubscript{1/2}MnO\textsubscript{3} [74] and RNiO\textsubscript{3} (R-rare earth) [75]. In these materials it is hard to observe the ferroelectric signal due to high background electrical conductivity. LuFe\textsubscript{2}O\textsubscript{4} also exhibits ferroelectricity due to charge ordering of Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, which lie on a bilayer structure and are frustrated by the underlying triangular lattice. The ratio of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} is 2:1 and 1:2 in the alternating triangular layers and charge transfer between these layers produces the ferroelectricity [76, 77, 64, 78].

2.6.4 GEOMETRICALLY DRIVEN FERROELECTRICITY

In some multiferroics, the ferroelectricity is not driven by the off center shift of transition metal cation in the lattice, which can occur in lattices supporting more complex distortions. One example of this mechanism is found in hexagonal RMnO\textsubscript{3} (R-rare earth) systems, where ferroelectricity is induced by the tilting of the MnO\textsubscript{5} bipyramids and the buckling of R-O plane simultaneously [69]. In hexagonal YMnO\textsubscript{3} the ferroelectricity is not due to magnetic Mn\textsuperscript{3+} ions but due to the tilting of MnO\textsubscript{5} block with Mn ion remaining at the center. This provides a closer packing of the ions and the resulting Y-O bonds form dipoles, leading to ferroelectricity [69]. BaMF\textsubscript{4} (M = Fe, Ni, Co and Mn) is another member of this group, where alternating rotations of the MF\textsubscript{6} octahedra in the bc-plane accompanied by the displacement of the Ba cations along the c-axis generates the ferroelectricity[79].
2.7 MICROSCOPIC ORIGIN OF FERROELECTRICITY, MAGNETISM, AND MAGNETOELECTRIC COUPLING IN TYPE-II MULTIFERROICS

Type-II multiferroics exhibit a form of improper ferroelectricity and are identified as magnetic multiferroics. In these systems, ferroelectricity is induced by inversion-breaking magnetic ordering. This class of multiferroics exhibit very large ME coupling, which is an important ingredient for device applications because of cross control of polarization by magnetic field and vice-versa. Some examples of type-II multiferroics are TbMnO$_3$ [72], TbMn$_2$O$_5$ [80], Ni$_3$V$_2$O$_8$ [70], FeVO$_4$ [71], DyMnO$_3$, DyMn$_2$O$_5$ [81], and CuO [82]. These multiferroics are further subdivided into two types: one in which ferroelectricity is driven by spiral magnetic structure and other where a collinear magnetic structure cause ferroelectricity [64].

2.7.1 MULTIFERROICS WITH SPIRAL MAGNETIC STRUCTURE

The spiral magnetic structure in RMnO$_3$ (R = Tb, Dy) magnetic multiferroics is the result of competition between nearest neighbour (NN) ferromagnetic and next nearest neighbour (NNN) antiferromagnetic superexchange interactions [81, 83]. Microscopic [84] and phenomenological [85] models have been used to explain the magnetically driven onset of ferroelectricity in these system. According to one microscopic mechanism, a spin current $\vec{J}_s$ arises in the presence of two coupled non-collinear spins $\vec{S}_1$ and $\vec{S}_2$ given by:

$$J_s \propto \vec{S}_1 \times \vec{S}_2$$  \hspace{1cm} (2.25)
Figure 2.13: Schematic representation of the microscopic mechanism of spin induced polarization for the spin current model [84]

The induced polarization is proportional to the cross-product of the spin current and the unit vector $\hat{e}_{ij}$ connecting the neighbouring spins $\vec{S}_1$ and $\vec{S}_2$. Thus

$$P \propto \hat{e}_{ij} \times \vec{J}_s$$  \hspace{1cm} (2.26)

Sergienko et al [86] explained this effect in terms of the inverse Dzyaloshinskii-Moriya (DM) interaction, where two non-collinearly coupled magnetic moments displace the oxygen atom located between them through an electron-lattice interaction. In these magnetic spiral structures, the displacement of oxygen ion is in the same direction due to the fact that all pairs of neighboring spins in the cross product of $\vec{S}_n$ and $\vec{S}_{n+1}$ have the same sign, as shown in Fig 2.13. When the exchange interaction between two spins is reversed, the sign of the effect in the asymmetric DM interaction is also reversed as $[\vec{S}_i \times \vec{S}_j = -\vec{S}_j \times \vec{S}_i]$. This explains why the sign of the electric polarization can be switched by a reversal of the spin spiral, as illustrated in Fig 2.14, showing the reversal of the polarization direction upon changing from a clockwise spiral to counterclockwise spiral.

In a phenomenological model[85] the symmetry of the electrical and magnetic dipole
Figure 2.14: Schematic representation of the change of local electric polarization induced by spin canting (a) in clockwise and (b) counterclockwise spiral spin structure and (c) spin canting AF spin structure [87]

moments is considered to explain the magnetically induced ferroelectricity. The magnetic dipole moments are reversed by time inversion and are unaffected by spatial inversion whereas electrical dipole moments are reversed by spatial inversion but are unaffected by time reversal. Thus linear coupling is possible only when both spatial inversion and time reversal are taking place simultaneously. The coupling between the polarization $P$, and magnetization $M$ must be nonlinear as a result of the interplay between charge, spin, orbital and lattice degrees of freedom [77, 85]. The ME coupling of biquadratic $-P^2M^2$ in nature is always allowed by symmetry [77, 85]. This has been observed in YMnO$_3$, noticing change in dielectric constant below magnetic ordering temperature [88]. The trilinear coupling term $PM\partial M$ is also allowed provided magnetization has gradient terms. This induces electric polarization as it is linear in $P$. The magnetically induced polarization for the case of cubic symmetry based on Mostovoy’s phenomenological model [85], derived from the Ginzburg-Landau symmetry theory, is given by:
\[ \vec{P} = \gamma \chi_e [\vec{M} \cdot \vec{\nabla}] \vec{M} - \vec{M} (\vec{\nabla} \cdot \vec{M}) \]  
(2.27)

where \( \chi_e \) is the dielectric susceptibility in the absence of magnetization. Frustration or competing interactions can introduce a spatial variation in \( M \) and gives rise to the spiral magnetic order. The onset of spiral spin order breaks spatial inversion and time reversal symmetry simultaneously and thus allows the coexistence of magnetic and ferroelectric order. The magnetic spin-spiral structure can be described by a spin density wave of the form:

\[ \vec{M} = M_1 \hat{e}_1 \cos(\vec{Q} \cdot \vec{x}) + M_2 \hat{e}_2 \sin(\vec{Q} \cdot \vec{x}) \]  
(2.28)

Where \( \hat{e}_1 \) and \( \hat{e}_2 \) are unit vectors for an orthogonal basis and \( \vec{Q} \) is the wave vector of the magnetic spiral. The spin rotation axis will be perpendicular to both \( \hat{e}_1 \) and \( \hat{e}_2 \) and is given by \( \hat{e}_3 = \hat{e}_1 \times \hat{e}_2 \). The magnetic induced polarization is perpendicular to both \( \hat{e}_3 \) and \( \vec{Q} \) and is given by

\[ \vec{P} = \gamma \chi_e M_1 M_2 (\hat{e}_3 \times \vec{Q}) \]  
(2.29)

Thus the magnetically induced polarization is proportional to \( M_1 \) and \( M_2 \) both. If \( M_1 \) or \( M_2 \) is zero, the resultant \( M \) will be a collinear sinusoidal state, which does not break the spatial inversion symmetry and thus spins will not be able to induce polarization i.e. ferroelectric order will not be allowed. However if \( M_1 \) and \( M_2 \) both are non zero, the resultant \( M \) will be a non-collinear spiral state, which can induce polarization if the spin rotation axis is perpendicular to the wave vector \( \vec{Q} \) [85]. This is shown in Fig 2.15, where the magnetically induced polarization is zero for the sinusoidal spin structure but a non-zero polarization develops for the non-collinear spin structure where the spin rotation axis \( \hat{e}_3 \) do not coincide with the spin wave vector \( \vec{Q} \).

The onset of ferroelectricity at magnetic ordering can also be explained by a phenomenological model proposed by Brooks Harris [8]. This model is based on Landau symmetry
Figure 2.15: Fig (a) the magnetically induced polarization is zero for sinusoidal spin structure and (b) non-zero polarization $\vec{P}$ is induced perpendicular to both the spin rotation axis $\hat{e}_3$ and the spin wave vector $\vec{Q}$ for the non-collinear spin structure [85]

analysis in the mean field approximation, which suggests that the spin structure can alone break the spatial inversion symmetry leading to ferroelectric order [8]. This model successfully explains the coexistence of long range ferroelectric and magnetic orders in geometrically frustrated materials such as Ni$_3$V$_2$O$_8$ [70], FeVO$_4$ [89], TbMnO$_3$, TbMn$_2$O$_5$ and similar systems as well [90]. The Landau free energy in terms of magnetic order parameters $\vec{\sigma}$, ferroelectric order parameter $\vec{P}$ and magnetoelectric energy $V_{ME}$ is expressed as:

$$f_{ME} = a\frac{P^2}{\chi_E} + b(T - T_M)|\sigma|^2 + V_{ME}$$

(2.30)

where $\chi_E$ is the electric susceptibility, $a$ and $b$ are constants and $T_M$ is the magnetic ordering temperature. For Ni$_3$V$_2$O$_8$, this expansion has been expressed as [8]:

$$f_{ME} = \frac{1}{2}(T - T_H)\sigma_H(q)\sigma_H^*(q) + \frac{1}{2}(T - T_L)\sigma_L(q)\sigma_L^*(q) + \vartheta(|\sigma|^4) + \frac{1}{2}\frac{P^2}{\chi_E} + V_{ME}$$

(2.31)
Where H and L represents the HTI (High Temperature Incommensurate) and LTI (Low Temperature Incommensurate) magnetic phases for Ni$_3$V$_2$O$_8$ system. The magnetoelectric energy $V_{ME}$ for LTI phase is given as:

$$V_{ME} = \sum_{\gamma} a_{\gamma} \sigma_H \sigma_L P_{\gamma}$$  \hspace{1cm} (2.32)

whereas for the HTI phase $V_{ME}$ is zero. The magnetically induced polarization can be obtained by minimizing free energy as:

$$P_{\gamma} = \frac{\partial f_{ME}}{\partial P}$$  \hspace{1cm} (2.33)

which gives

$$P_{\gamma} \propto a_{\gamma} \chi_E \sigma_H \sigma_L$$  \hspace{1cm} (2.34)

This explains how two non-zero magnetic order parameters $\sigma_H$ and $\sigma_L$ in the LTI phase of Ni$_3$V$_2$O$_8$ are necessary to produce the electric polarization. Further considering the group theoretical crystal symmetries allows the prediction that the polarization can only along b-axis [70], which is confirmed by experiment. A very similar Landau theory has been developed for FeVO$_4$ [71] where the crystal symmetry does not impose any restriction on the direction of magnetically induced polarization.

### 2.7.2 MULTIFERROICS WITH COLLINEAR MAGNETIC STRUCTURE

In this class of multiferroics, the ferroelectricity is driven by a collinear magnetic phase. In this collinear magnetic phase all magnetic moments are aligned along a particular direction without involving the spin orbit interaction. The magnetically induced polarization in these systems is due to the exchange striction because the magnetic coupling varies with atomic positions. The recently discovered Ca$_3$CoMnO$_6$ multiferroic [91] exhibit this be-
Figure 2.16: Schematic representation of the polarization $\vec{P}$ induced by simultaneous charge ordering and dimer type Ising spin chain. Exchange striction shifts cations away from their centrosymmetric positions [77]

behaviour. This consists of 1D chains of alternating Co$^{2+}$ and Mn$^{4+}$ ions. Above the magnetic ordering temperature, the distance between ions along chain is constant, which does not favour polarization. However, below the magnetic ordering temperature, a combination of alternating charge ordering of transition metal ions of different valence, a similar situation as explained in “Electronic Ferroelectricity” section, and an Ising-like magnetic structure $\uparrow\uparrow\downarrow\downarrow$ can give rise to ferroelectricity via exchange striction. This exchange striction is due to competition between nearest neighbour (NN) ferromagnetic and next nearest neighbour (NNN) antiferromagnetic superexchange interactions. The shorter distance between cations with parallel spins and longer distance between cations with anti-parallel spins break the inversion symmetry for the system and gives rise to the polarization along the chain Fig 2.16.
Beyond these type-I and type-II single phase multiferroics, there are multiphase materials exhibiting multiferroic properties. In order to produce any magnetoelectric coupling, one of the two phases should be piezomagnetic or magnetostrictive and the other should be piezoelectric or electrostrictive. The magnetic and ferroelectric properties of these materials can be tuned independently and the restriction of ME coupling Eq. (2.23) is not valid. The coupling in such systems takes place indirectly via strain, for which intimate contact between two phases is required. Usually ferroelectric in combination with ferromagnets are used for such systems. These systems can be put into contact in the form of composites, laminates or epitaxial multilayers [53]. The coupling coefficients in these systems are relatively large in comparison to the single phase multiferroics.

Any practical application of multiferroics depends on the development of materials having higher ordering temperatures with larger magnetoelectric couplings. While type-I multiferroics exhibit high temperature magnetic and ferroelectric ordering, they generally have smaller ME couplings. Conversely, type-II multiferroics exhibit large ME coupling only at their low ordering temperatures. There is an open quest to search or design/engineer a single phase multiferroic exhibiting large ME coupling at high temperatures. The realization of these materials in thin film form is also desirable, as a small applied voltage can give rise to very large electric field, which is not possible for the bulk system. This can give rise to new type of voltage controlled devices [8].
Chapter 3

III-NITRIDES AND RELATED DILUTE MAGNETIC SEMICONDUCTORS (DMSs) - OPTICAL, ELECTRONIC AND MAGNETIC PROPERTIES

3.1 INTRODUCTION

III-nitrides consist of alloys of group III elements with the smallest group V element, Nitrogen. Aluminum (Al), gallium (Ga) and indium (In) are the main group III elements, which constitute most III-nitrides. Among these, gallium nitride (GaN) is the binary representative to its sister compounds aluminum nitride (AlN) and indium nitride (InN) together with their ternaries and quaternaries. The wurtzite crystal structure of all three binary AlN, GaN and InN compounds allow the possibility of alloying homogeneously ternary Al$_{1-x}$In$_x$N,
Ga$_{1-x}$In$_x$N and quaternary Al$_{1-x-y}$Ga$_x$In$_y$N solid solutions for $0 < x < 1$ and $0 < y < 1$. The presence of a direct bandgap and the fact that this can be tuned from 0.7 eV ($E_g$ for InN) to 6.2 eV ($E_g$ for AlN) make these nitride semiconductors ideal for a range of applications including short wavelength light emitters, which are essential for full colour display, high density information storage, and underwater communications [1]. These systems are also suitable for optoelectronic devices in the violet and blue region of the electromagnetic spectrum with respect to other conventional III-V semiconductors. These devices include laser diodes (LDs), light emitting diodes (LEDs) among others. InGaN based LEDs are in use for full colour display, commercial lights and LDs in CD/DVDs for high density read/write applications [1, 2].

The wide band gap of these nitride semiconductors (with the exception of InN) and strong bond strength, which are responsible for the mechanical properties of these compounds, make these materials more suitable for high temperature electronic devices than many other compound semiconductors. These nitride semiconductors have good thermal conductivity [92]. Binari et al [93] and Duboz et al [94] have shown that $III - N$ devices can operate at both high temperatures and under hostile environments. These make $III - N$ useful for high temperature and high power transistors, automobile applications, all electric vehicles, and avionic electronics [1].

The recent findings of low band gap for InN (0.7eV) and combined with alloying with GaN made it possible to engineer the bandgap from 0.7 eV to 3.4 eV for In$_{1-x}$Ga$_x$N, as shown in Fig 3.1. Varying the Ga content in a In$_{1-x}$Ga$_x$N alloy can cover the entire solar spectrum from near infrared to ultraviolet, as shown in Fig 3.1, which may lead to new multijunction (MJ) tandem solar cells having improved efficiency as compared to conventional cells using Ge, GaAs and GaInP multilayers [22]. The interface between different active layers in a conventional MJ solar cells often includes interfacial defects creating more scattering centers for carriers, which hampers the device performance and efficiency. These interface
related defects can be minimized/avoided using a InGaN alloy with different Ga atomic concentrations. An analogous system, InAlN, can be utilized for such devices. The mechanical strength and radiation resistive properties of these nitrides offer enormous potential for space solar cell applications [22, 95].

**CRYSTAL STRUCTURE AND ELECTRONIC PROPERTIES**

The electronic properties of a material usually depends on the crystal structure and valence electrons and are responsible for various optical and transport phenomenon. The structural and electronic properties of III-nitride semiconductors are reviewed in detail in references [1, 2, 96, 97]. In general, III – Ns can crystallize into the wurtzite, zinc blende and rock salt (NaCl) structures. The wurtzite crystal structure, as shown in Fig 3.2, is the only thermodynamically stable phase of III-nitrides (AlN, GaN and InN) under ambient conditions.
This wurtzite structure consists of two interpenetrating hexagonal close packed sublattices, each with one type of atoms either group III-element or nitrogen with an offset along the c-axis by 5/8 of the cell height (5c/8) and belong to the $C_{6v}^4$ ($P6_3mc$) space group with $6mm$ point group symmetry. Here, nitrogen atoms form a hexagonal close pack structure and half of the tetrahedral sites are occupied by group III-elements in the crystal lattice, Fig 3.2 and 3.3. III-nitrides in wurtzite structure form a layered structure with atoms in hexagons follow the sequence $\text{III}_A\text{N}_A\text{III}_B\text{N}_B\text{III}_A\text{N}_A\text{III}_B\text{N}_B......$ along the [0001] axis, as shown in Fig 3.3(a), where each group III element is coordinated by four nitrogen atoms and each nitrogen atom is coordinated by four group III atoms. The zinc blende structure of group III-nitride is a metastable phase and crystallizes into the cubic unit cell where atoms follow the sequence $\text{III}_A\text{N}_A\text{III}_B\text{N}_B\text{III}_C\text{N}_C\text{III}_A\text{N}_A\text{III}_B\text{N}_B\text{III}_C\text{N}_C....$ along the [111] direction, as shown in Fig 3.3(b). This crystal structure belongs to the $T_d^2$ ($F\bar{4}3m$) space group. The zinc blende structure for GaN and InN has been stabilized by epitaxial growth of thin films.
Figure 3.3: Stick and ball model of wurtzite and zinc blende crystal structures. Figures at the bottom indicate the projections onto the (0001) and (111) planes for wurtzite and zinc blende respectively [99].
Figure 3.4: Energy bandgap versus in-plane lattice constant of III-nitrides and other semiconductors [99].

on 011 cubic substrates of Si [100], SiC [101], MgO [102] and GaAs [103]. In this case the topological compatibility overcomes the barrier of forming the cubic structure. The rock salt crystal structure of group III-nitrides belongs to the $O_\beta^5$ ($Fm\bar{3}m$) space group and can be induced only under very high pressure. The high pressure reduces the lattice dimensions which causes the interionic Coulomb interaction to favour the ionicity over the covalent nature [99].

The energy bandgap of group III-nitrides and various other semiconductors is shown in Fig 3.4 [99]. The bandgap energies of III-N materials cover the entire solar electromagnetic spectrum ranging from the infrared (IR) to the ultraviolet (UV) region. Among group III-nitride semiconductors InN is perhaps the most perplexing system. The recent observations
of a low bandgap in InN, $\sim 0.7$eV, much smaller than previously accepted bandgap $\sim 1.9$eV, has attracted considerable interest for possible applications in the infrared $^{[22]}$. Additionally InN is predicted to have the lowest effective mass for electrons among all nitride semiconductors, approximately half that of GaN, which gives rise to a high mobility and a high saturation velocity for the electrons. The theoretical mobility calculated in InN and GaN at 300 K are 4400 and 1000 $cm^2V^{-1}s^{-1}$ respectively, while at 77K the limits are beyond 30000 and 6000 $cm^2V^{-1}s^{-1}$ respectively $^{[2]}$. The peak drift velocity and saturation velocity are much larger than those of GaAs and GaN, as shown in Fig 3.5 (b) $^{[2]}$. Therefore, it is expected that InN films should have better performance for high frequency devices than GaN. Alloying of InN with GaN and AlN will produce ternary compounds InGaN and InAlN, where bandgap energy can be tailored from 0.7 eV to 3.4 eV and 6.2 eV respectively.

In spite of these promising predictions for their electronic and optical properties, InN thin film semiconductors do not consistently show good behaviour. There are various unexplained
issues regarding this material. Some of those are discussed below briefly.

**BANDGAP CONTROVERSY OF InN**

In contrast to GaN and AlN, the electronic properties of InN remain highly debates, especially the value of the electronic bandgap. The electronic bandgap of InN thin films was believed to be $\sim 1.9$ eV [15, 105, 106]. More recent studies showed a bandgap of $\sim 0.7$ eV [17, 107, 18, 108]. Thus, depending on the preparation method and film quality, a wide range 0.7-1.9 eV of electronic bandgap values have been reported in the literature. These are summarized in Fig 3.4. The higher values of the bandgap (1.8 - 2.3 eV) have been determined from optical absorption measurements on polycrystalline or (0002) textured InN films deposited by reactive sputtering [15]. Absorption and photoluminescence measurements on InN films grown on (0001) sapphire substrates by MBE (molecular beam epitaxy) [18] and MOVPE (metalorganic vapor phase epitaxy) [108] have shown smaller bandgap values (0.7-1.0 eV). These lower bandgap values are associated with improvements in the film structure, which have fewer defects and lower carrier concentrations. These values are also consistent with theoretical values [109, 110]. The higher bandgap in radio frequency (RF) sputtered thin films is attributed to the incorporation of oxygen during fabrication. It has been proposed that a high oxygen concentration in these films leads to the formation of an InN-In$_2$O$_3$ alloy, which may have a higher bandgap than the intrinsic band gap of InN because of high bandgap of value of In$_2$O$_3$ ($\sim 3.75$ eV) [111, 112]. Recently Shubina et al proposed that the photoluminescence peak at 0.7-0.8 eV from films grown by MBE and MOCVD, may be due to Mie scattering from metallic indium clusters [113]. These cluster may originate during film growth, particularly above 500°C. The absorption edge was shown to drop with a decreasing concentration of In clusters. The absorption edge was reported to be $\sim 1.4$ eV for a film with no In clusters [113]. The smaller band gap ($\sim 0.7$ eV) also seems to violate the common cation rule, which suggests that the bandgap of a semiconductor
increases as the atomic number decreases. The atomic orbital energies, their differences and bandgap deformation potentials in the InN system led to smaller band gap and suggests that common-cation rule does not hold for InN [114, 115, 116]. Establishing the correct value of the band gap for InN is crucial, as the usefulness of this material for particular applications depends sensitively on the exact value of the band gap. For example, if the bandgap is around \( \sim 2 \) eV, InN may be useful in high frequency devices, whereas a low bandgap closer to 0.7 eV may be useful for various infrared, optoelectronic and photovoltaic applications.

SURFACE ELECTRON ACCUMULATION IN InN SYSTEM

Another associated challenge in the InN system is the unavoidable surface electron accumulation, which forms an intrinsic two-dimensional electron gas with very high electron concentration of the order of \( 10^{21} \text{ cm}^{-3} \) and is confined to a very small thickness close to the surface \( \sim 5 \text{nm} \) [117, 19, 118]. This surface accumulation layer modifies the bulk properties. Recently it has been shown that this intrinsic electron accumulation at the surface of InN thin films is due to the pinning of Fermi level at \( \sim 0.8 \) eV above the conduction band minimum because of intrinsic surface states [119, 120]. This surface layer can not be avoided by thinning or etching the film, the n-type layer just reforms wherever a new surface is provided, as surface dangling bonds are prone to donate electrons easily. Usually, this surface electron accumulation layer is not desired for many electronic devices. However, this property may be useful for some specific device applications e.g. sensors, terahertz emitters, spintronics devices and semiconductor/superconductor hybrid devices [120, 121].

NATIVE DEFECTS AND INTRINSIC HIGH ELECTRON CONCENTRATION IN InN SYSTEM

In general, undoped InN thin films show very high electron concentration \( \sim 10^{21} \text{ cm}^{-3} \) [111, 112]. Such high carrier concentrations in InN thin films is responsible for partially
filling the conduction band. This causes a shift in the observed optical absorption edge and obscures estimates of the true band gap. This shift in the band edge, due to pinning of Fermi level into the conduction band is known as the Moss-Burstein shift [122, 123]. This Moss-Burstein shift is evoked to justify the high band gap often observed \( \sim 1.9 \) eV of InN system [22, 124, 16]. The reason for such a high carrier concentration is unclear. The main impurities responsible for this unintentional n-type conductivity are assumed to be oxygen and hydrogen [125, 126]. These unavoidable impurities are generally introduced during growth or the post-growth processing. Additionally nitrogen vacancies are also believed to be responsible for unintentional electron donor in the InN system [127]. The formation energy of various native point defects e.g. indium and nitrogen antisites, vacancies, interestials and impurities e.g. oxygen, silicon, magnesium etc in the InN host matrix has been reviewed in many articles [127, 111]. Stoichiometric conditions are necessary to ensure when contemplating the nature of defects in the host. For example, in stoichiometric InN, the formation energy of antisite defects is the lowest among defects, whereas under nitrogen and indium rich conditions, the formation energy of nitrogen interstitial defect and nitrogen vacancy defects are the smallest respectively. Thus, the main source of a high concentration electron carriers in InN is either nitrogen interstitials or vacancy in N-rich or In-rich conditions respectively [112]. In as grown InN, the formation energies of such native point defects are much higher in comparison to the formation energies of oxygen defects, which is a very common contaminant. More interestingly, recent findings indicate that hydrogen in InN behaves as a donor in contrast to GaN and AlN where it behaves as an amphoteric defect [126]. This explains the nature of complex nature of intrinsic defects and contaminants in InN, suggesting that the degenerate nature of InN thin films may be mostly due to unavoidable oxygen and hydrogen.
CONTROVERSY OVER THE COUPLED MODES IN InN DUE TO A1(LO) AND PLASMON IN THE SYSTEM

In a polar semiconductor, the longitudinal optical (LO) phonons may couple to the collective oscillations of the free carriers, plasmons, and are expected to occur in InN because of the polar nature of the wurtzite-crystal structure. This should result into the development of two coupled modes in InN films - a high energy plasmon-LO phonon ($PLP^+$) coupled mode and a lower energy plasmon-LO phonon ($PLP^-$), coupled mode. These modes can be observed in the Raman and infrared (IR) spectra if they are not damped. The presence of such coupled modes has been observed in other group III-nitride semiconductors such as GaN [128]. However, these coupled electron-LO modes have not yet been found in InN films.

CHALLENGES IN p-TYPE DOING IN InN SYSTEM

For any possible realization of InN based optoelectronic devices, the development of p-type InN is essential. As mentioned previously, intrinsic InN suffers from unintentional n-type doping and surface electron accumulation. These difficulties make it difficult to prepare p-type InN. More recently, p-type InN has been developed using Mg acceptors in the host, where Mg doped InN films exhibit p-type conductivity due to acceptors below the n-type surface [129]. The bandgap energy of III-nitrides with respect to the Fermi level stabilization ($E_{FS}$) energy is shown in Fig 3.5(b)[104], where the Fermi level stabilization energy ($E_{FS}$) is the measure of average dangling bond energy after defects are introduced. For InN, as shown in Fig 3.5(b), $E_{FS}$ is located $\sim$ 1.5 eV and $\sim$ 0.8 eV above the valence and conduction bands respectively. Additionally, recent electron energy loss spectroscopy (EELS) studies confirmed the energy level of $E_{FS}$, indicating that the Fermi level is pinned $\sim$ 1.64 eV above the valance band edge [117]. The unintentional dopants providing excess carriers in InN cause this Fermi level pinning and can be explained by the amphoteric defect model (ADM) developed by Walukiewicz [104]. This model suggests that the doping properties (p
or n type) of semiconductors depend on the position of valence and conduction band energy levels compared to the average energy of a defect in the crystal and that the type of dominant native defects (donor or acceptor) depend on the location of the Fermi energy $E_F$ relative to the $E_{FS}$. When $E_F$ is less than $E_{FS}$ (or $E_F$ is greater than $E_{FS}$), the formation energy of charged donor (or acceptor) defect is reduced, and native defects in the system tend to be donor (or acceptors). The conduction band of InN is usually low in energy and lies below the average defect energy levels, Fig 3.5(b). This, in general, results into the n-type InN. Thus low formation energy of native donor defects in InN makes the formation of p-type InN more difficult. Additionally the surface electron accumulation layer in InN thin films severely affects the electrical measurements. Thus the development of p-type InN requires the effective suppression or termination of surface electron accumulation layer and reduction of donor impurity defects in the system.

The influence of oxygen on InN is rather complex as discussed above. In following sections, we will discuss the influence of oxygen contamination on the structural and optoelectronic properties of InN films and will explore the possible applications of highly degenerate RF sputtered InN thin films.

### 3.2 EXPERIMENTS AND RESULTS

#### 3.2.1 FABRICATION OF InN, $\text{In}_1-x\text{Ga}_x\text{N}$ and $\text{In}_1-x\text{Cr}_x\text{N}$ THIN FILMS

Motivated from the complex nature of oxygen defects and in order to understand the changes in InN structural/microstructural and optoelectronic properties, we prepared InN thin films using high purity (5N) In metal and In$_2$O$_3$ targets. The In$_2$O$_3$ powder (99.99%) was mixed homogeneously with 15 ml of 2M polyvinyl alcohol (PVA) solution in deionized (DI) water as a binder. This homogeneously mixed In$_2$O$_3$ powder was pressed into a circular
disc of ∼30 mm diameter and followed by air annealing at 1000°C for 12 hours. The InN thin films under investigation were deposited using RF magnetron sputtering system onto (0001) sapphire substrates. The detailed RF magnetron sputtering process is explained in appendix.

The sputtering chamber was maintained at a base pressure of ∼10⁻⁶ torr for more than 24 hours to avoid undesired contaminants inside the sputtering chamber. The substrate was preheated under high vacuum before introducing any reactive/sputtering gas into the chamber and maintained at a constant film growth temperature as shown in Fig 3.6. A mixture of high purity nitrogen, as a reactive gas at a partial pressure of 5 × 10⁻³ torr and argon as a sputtering gas with total working pressure of 1.5 × 10⁻² torr was used for the InN thin film fabrication. We presputtered the sputtering targets for ∼30 minutes to remove the possible surface contaminants prior to any thin film deposition. The deposition conditions were kept identical for the InN thin films prepared from In metal and In₂O₃ targets and thickness of these thin films were maintained ∼1 μm. We also prepared 2% and 5% Cr doped InN thin films using stoichiometrically 2% and 5% Cr doped In₂O₃ targets. These targets were prepared by adding chromium chloride (CrCl₃.6H₂O) powder into In₂O₃.
powder in appropriate Cr to In atomic ratio 2:98 and 5:95 for 2\% and 5\% Cr doped In$_2$O$_3$ targets respectively. These powders were mixed in ethanol to ensure homogeneously mixing. This powder was heated at 600\°C for 12 hours. This process of homogeneously grinding and heating was repeated 4 times to complete the solid state reaction. This solid solution was then mixed with PVA binder with a ratio of 1ml 1M PVA solution in DI water for 1g powder and hydraulically pressed into a circular disc of \(\sim 30\) mm diameter. These circular discs were finally heated at 1000\°C for 12 hours before using as sputtering targets. The fabrication process for In$_{1-x}$Cr$_x$N thin films is very similar to the InN thin film deposition process discussed above. The only difference was that we used only N$_2$ as both reactive and sputtering gas for depositing these films.

The In$_{1-x}$Ga$_x$N thin films used in this study were grown at \(\sim 470\)\°C by molecular beam epitaxy (MBE) technique at Cornell University [124, 130] on c-axis sapphire substrates. In order to minimize the lattice mismatch between the In$_{1-x}$Ga$_x$N and sapphire substrate, additional buffer layers of \(\sim 10\) nm AlN followed by \(\sim 200\) nm GaN on (0006) sapphire substrates were grown before In$_{1-x}$Ga$_x$N thin film deposition. The film thickness was maintained \(\sim 0.5\) \(\mu\)m.

### 3.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF InN AND In$_{1-X}$Cr$_X$N THIN FILMS

We have investigated the structural and microstructural properties of these thin films using X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The X-ray diffraction patterns (XRD) of InN films prepared from metal target (InN-MT) and the oxide target (InN-OT) are shown in Fig 3.7.

The InN-MT film is highly textured along the c-axis, as shown in Fig 3.7(a), where diffraction peaks at \(2\theta = 31.43^\circ\) and 65.4\° correspond to (002) and (004) wurtzite InN reflections. The InN film prepared from the oxide target (InN-OT) shows multiple broad
Figure 3.7: XRD pattern for (a) InN-metal film and (b) InN-oxide film. “*” indicates the peaks due to the Al\textsubscript{2}O\textsubscript{3} (0006) reflection. HRTEM images of (c) InN-metal and (d) InN-oxide thin films. In (c) “G” shows the grain boundary region between the highly oriented InN columnar crystals. In (d) areas marked with letters “a” and “c” indicate the disordered amorphous and crystalline regions within the InN crystallites.
reflections at $2\theta = 28.96^\circ, 30.66^\circ$ and $32.85^\circ$, indicating an isotropic polycrystalline sample. The structural refinement for both films was carried out and the values of lattice parameter $c$ are 5.711 Å and 5.817 Å for InN-MT and InN-OT respectively. The large value of $c$ and hence $c/a$ for InN-OT films suggests the existence of large lattice distortions and associated defects, unlike the InN films where the lattice parameters are in good agreement to the reported values in the literature [112]. Additionally, the representative XRD patterns of InN thin films deposited under different conditions, discussed in detail in [131], is shown in Fig 3.8(a), where top panel represents XRD pattern for InN film with the lowest carrier concentration and lower panel for InN films with highest carrier concentration. These XRD patterns indicate a polycrystalline nature of InN thin films, although films are highly textured along c-axis.

The crystal structure and stoichiometry of 2% and 5% Cr doped $\text{In}_{0.98}\text{Cr}_{0.02}\text{N}$ and $\text{In}_{0.95}\text{Cr}_{0.05}\text{N}$ thin films was determined using X-ray diffraction and SEM-EDX respectively. The XRD patterns for both films are shown in Fig 3.9. All the peaks in the XRD plots can be indexed to the hexagonal wurtzite InN crystal structure, consistent with the polycrystalline nature of these films. The atomic concentration of Cr in these thin film was estimated using the energy dispersive X-ray analysis (EDX) accessory associated with the scanning electron microscope (SEM) and the observed atomic concentrations are in good agreement with our estimated 2% and 5% Cr atomic fraction in $\text{In}_{0.98}\text{Cr}_{0.02}\text{N}$ and $\text{In}_{0.95}\text{Cr}_{0.05}\text{N}$ thin films respectively. We do not observe any conventional magnetic impurities, Cr clustering or $\text{Cr}_2\text{O}_3$, from the XRD patterns for these thin films, consistent with our microstructural and magnetic studies, which are discussed in detail in the following sections. More remarkably we do not find trace of $\text{In}_2\text{O}_3$ secondary phases in XRD pattern, even these sample were prepared using Cr doped $\text{In}_2\text{O}_3$ targets, consistent with our previous studies [132].

In order to further investigate the microstructural investigation of these thin films, we carried out cross-sectional scanning electron microscopy (SEM) and high resolution trans-
Figure 3.8: (a) XRD pattern for InN thin films having the lowest (top panel) and highest (lower panel) carrier concentrations. "*" indicates the peak due to the Al₂O₃ (0006) reflection. The small anomaly in the top panel near 35° represents an instrumental error. (b) Cross-sectional SEM micrograph of InN/Sap thin film. HRTEM images of (c) the lowest and (d) highest carrier concentration InN thin films.

Figure 3.9: XRD pattern of In₀.₉₉₉Cr₀.₀₂N/Sap (bottom panel) and In₀.₉₉₅Cr₀.₀₅N/Sap (top panel)
mission electron microscopy (HRTEM). A representative cross-sectional SEM micrograph is shown in Fig 3.8(b). The cross-sectional SEM micrographs were also used to estimate thicknesses of InN thin films. The HRTEM images for InN-MT and InN-OT thin films are shown in Fig 3.7(c) and 3.7(d) respectively. The InN-MT films show highly c-axis oriented columnar grains. These columnar grains are $\sim 1\mu m$ in length and $\sim 60$ nm in width. InN-MT film is free from any structural defects within individual columns and separated by grain boundaries marked as G in Fig 3.7(c). The InN-OT films consist of a number of disordered/amorphous regions marked by a and crystalline regions indicated by c, are $\sim 5-8$ nm in diameter, Fig 3.7(d). In addition, representative HRTEM images of InN thin films prepared from the In metal target under different conditions [131] are shown in Fig 3.8(c) and 3.8(d). These HRTEM images suggests highly oriented columnar grains of InN for these films, in agreement with our XRD results.

3.2.3 PHASE SEPARATION AND OPTICAL PROPERTIES IN OXYGEN RICH InN THIN FILMS

As mentioned in the introduction, oxygen impurities in III-nitrides are almost unavoidable and cause n type behaviour in these systems. Additionally, the large band gap $\sim 1.8-2.1$ eV in reactively sputtered system has been attributed to the oxynitrides formed by the incorporation of oxygen in InN or due to band filling effects in the highly degenerate InN samples. We prepared InN thin films using In metal and In$_2$O$_3$ targets as discussed in section 3.2.1. The structural and microstructural investigation on these thin films are presented in section 3.2.2. We observe that InN thin films prepared from In$_2$O$_3$ target are more polycrystalline in nature with large number of defects in comparison to InN thin films prepared using In metal target as shown in Fig 3.7(c) and 3.7(d). In order to investigate further the effect of oxygen in these InN thin films, the relative elemental concentration of In, N and O in these InN thin films was analyzed using x-ray photoelectron spectroscopy (XPS).
AlKα (1486.6eV) radiation and an $Ar^+$ ion sputter etching process was used for the depth profile elemental analysis. The core level spectrum of In3$d_{5/2}$ and O1$s$ for both InN-MT and InN-OT films are shown in Fig 3.10(a)-(d). The In3$d_{5/2}$ spectrum can be deconvoluted into two peaks at $444.60 \pm 0.02$eV and $443.50 \pm 0.004$eV for both InN-MT and InN-OT films, as shown in Fig 3.10(a) and (b). The low energy peak at $443.50$ eV is associated to the electron binding energy of In in InN while the higher energy peak at $444.60$ eV can be attributed to the binding energy of In in In$_2$O$_3$ [133].

The surface of both the InN-MT and InN-OT films are oxygen contaminated and the surface oxygen elemental profile can be deconvoluted into two peaks at $532.00 \pm 0.02$eV and $530$ eV, where the higher binding energy peak at $532.00$ eV is due to adsorbed oxygen on the surface, and vanishes after etching to a depth of 1 nm. The low energy peak at $530$ eV is invariant as a function of depth and is associated to the BE of O, consistent with In-O coordination from a In$_2$O$_3$ secondary phase [134] in the InN matrix. The depth variation of the elemental concentrations is shown in Fig 3.10(e) and (f) for InN-MT and InN-OT thin films respectively. The decreasing N/In ration on sputtering in these samples can be attributed to the small binding energy of N to In, which leads to the preferential etching of N during sputtering [135]. The relative oxygen concentration of oxygen in InN-OT films is twice to that of InN-MT films, as shown in Fig 3.10(c) and (d), indicating the presence of higher concentration of In$_2$O$_3$ in InN film deposited from oxide target.

We conducted room temperature Raman spectroscopy experiments to investigate the effect of defects and distortions mediated by the excess oxygen into the InN. The Raman spectra for both the InN-MT and InN-OT films are shown in Fig 3.11(a) and (b). The expected $E_2$(low), $E_2$(high) and $A_1$(LO) modes near 90, 490, and 58 $cm^{-1}$ are observed for both films, indicating a c-axis orientation for the InN crystallites. These peaks are relatively sharper for InN-MT as compared to InN-OT, indicating InN-MT films are more highly textured. In addition to these possible InN Raman modes, we also observe peaks at $\sim$128,
Figure 3.10: X-ray photoelectron spectrum (XPS) of In3d$_{5/2}$ after 10 nm etching for (a) InN-metal and (b) InN-oxide thin films. O1s spectrum for the (a) and (b) are shown in (c) and (d). The atomic (%) concentration of In, N and O below the surface of (e) InN-metal and (f) InN-oxide films.
305, and 370 cm$^{-1}$ in the Raman spectrum of both the films, indicated with * in the spectrum. These correspond to the characteristic modes of bcc-structured In$_2$O$_3$ [136]. An unassigned mode $\sim$200 cm$^{-1}$ is also observed for both films with a larger intensity in the InN-OT films. This band could be a disorder activated B1 Raman mode of InN lattice, which is a silent Raman mode for InN crystal lattice but which has been reported for disordered/defective InN thin films. An infrared active phonon mode $\sim$218 cm$^{-1}$ is also also reported for In$_2$O$_3$, consistent with a possible violation of the Raman selection rules in defective systems. The presence of additional In$_2$O$_3$ phonon modes at 471, 504 and 630 cm$^{-1}$ could be a source of broadening of the InN E$_2$(high) and A$_1$(LO) modes observed in InN-OT thin films. The observed intensities of the In$_2$O$_3$ modes are higher in the InN-OT films than in the InN-MT films, consistent with the XPS study on these samples. This In$_2$O$_3$ secondary phase is mainly localized in the grain boundaries and disordered/amorphous region of the InN-OT films and only in the grain boundaries of InN-MT films.

We also carried out UV-Vis-NIR transmittance/reflectance, photoluminescence and Hall effect measurements on these thin films to investigate the effect of additional oxygen on the electrical and optical properties of InN thin films. The room temperature optical reflectance spectra for InN-MT and InN-OT films are shown in Fig 3.11(c) and (d), with the insets showing the corresponding room temperature photoluminescence (PL) spectra. The PL spectrum shows a strong and broad peak at $\sim$1.85 eV, consistent with the optical absorption edge obtained using the transmission and reflectance data for these films. The reflectance of these films was simulated using the Drude model, with the plasmon frequency ($w_p$) and the damping constant ($\gamma$) used as fitting parameters. The details of the fitting process and parameters are covered in reference [132]. The estimated values of the plasmon frequencies are $w_p$ $\sim$0.7 eV for both samples with different gamma values $\sim$0.043 eV and 0.087 eV for InN-MT and InN-OT films respectively. The room temperature carrier concentration of InN-MT and InN-OT films was determined by Hall effect measurements. The observed
Figure 3.11: Raman spectra of (a) InN-metal and (b) InN-oxide thin films. "**" indicates modes at 219 and 303 cm\(^{-1}\) from In\(_2\)O\(_3\). Reflection spectra for InN films (a) and (b) are shown in (c) and (d). The solid curve is experimental data and the dashed curve is theoretical fit. The insets to (c) and (d) show the photoluminescence spectra, which exhibit broad peaks near 1.85 eV corresponding to the optical absorption edge of the samples. The sharp feature at 1.8 eV in the inset to (d) is due to the sapphire substrate, while the sharp peak at 2.4 eV is the first order Raman spectrum signal.
carrier concentrations for InN-MT and InN-OT are $\sim (9 \pm 1) \times 10^{20} cm^{-3}$ and $(9 \pm 0.5) \times 10^{20} cm^3$ respectively. These values are consistent with the plasmon frequency estimated form the reflectance measurement for both films. Thus we find evidence for similar carrier concentrations for both films even though the InN-OT film has twice the oxygen content of the InN-MT sample.

These observations on InN-MT and InN-OT suggest that a small concentration of oxygen will likely form point defects distributed homogeneously in the InN host matrix [16, 17]. The formation energy of oxygen point defect inside the InN lattice includes contributions from the structural relaxation energy, the local chemical energy and the energy required to add an additional electron to the conduction band. The contribution from the first two terms are approximately independent of oxygen concentration for small concentrations. However each additional oxygen atom changes the electron chemical potential by injecting an additional electron into the conduction band. At sufficiently high impurity concentrations, the energy cost to incorporate oxygen homogeneously into the InN matrix as point defects can become very high, leading to the development of secondary phases. Our measurements suggest that the formation of an In$_2$O$_3$ secondary phase in addition to the InN$_x$O$_y$ phases identified previously [112]. This In$_2$O$_3$ secondary phase appears to nucleate along grain boundaries in higher quality InN samples, but can be distributed more homogeneously in disordered samples. This additional oxygen in In$_2$O$_3$ secondary phases will not donate electrons and thus will not increase the carrier concentration, which saturates after reaching a the limit set by the formation of oxygen point defects in InN.

We have investigated the effects of excess oxygen incorporation into the InN host matrix by studying the InN films prepared from In metal and In$_2$O$_3$ oxide targets. Raman analysis shows the presence of In$_2$O$_3$ secondary phases in both films, with an indication of higher oxide impurity in the InN-OT films. XPS elemental analysis of these films confirms the Raman results and shows that the oxygen concentration in the InN-OT film is approximately twice
that found in the InN-MT samples. The secondary In$_2$O$_3$ phase is mostly localized in the grain boundaries in the InN-MT films but can also be located in the disordered/amorphous regions within the InN crystallites in the InN-OT films. Hall effect measurements and optical reflectance measurements confirm that both films have similar carrier concentrations suggesting that beyond a certain concentration of oxygen, the oxygen rich InN lattice becomes unstable with respect to the formation of an In$_2$O$_3$ impurity phase leading to phase segregation, where the homogeneous In-N-O system separates into InN and In$_2$O$_3$ phases.

3.2.4 STRONG PLASOM ABSORPTION IN RF SPUTTERED InN THIN FILMS

The rf sputtered InN thin films are prone to exhibit a highly degenerate nature because of various defects introduced during growth. The oxygen incorporation into rf sputtered InN thin films is one of the most prominent source of contaminants and is identified as one of the possible source of donors in the InN system, as discussed in the sections above. The high carrier concentration in these lower quality thin films is contraindicated for many device applications, yet these degenerate samples can exhibit intense plasmon excitation similar to plasmons in metal. Therefore, under resonance conditions i.e. when plasmon frequency of an InN thin film coincides with an incident optical/infrared signal, these highly degenerate films can exhibit strong absorption. The absorption cross-section for plasmon excitations is small, however, if the absorption coefficient for the plasmon excitation can be increased as to the level of direct band gap excitation of electrons, then plasmon excitations could potentially be used for a number of applications where direct band gap absorption are currently used. Plasmon excitation absorption offers an additional advantage over direct bandgap absorption as the frequency response can be tailored continuously by varying the carrier density. Motivated from such applications, we studied highly degenerate InN thin films as a possible plasmon filter material in thermophotovoltaic systems [137] and in other
optical applications.

We fabricated InN/Sapphire thin films for five different carrier concentrations ranging from $3.84 \times 10^{20}$ to $1.26 \times 10^{21} \text{cm}^{-3}$. The synthesis details, growth parameters and various physical properties are discussed in table I of reference [131]. The representative X-ray diffraction pattern and microstructural cross-sectional SEM micrograph and high resolution images are shown in Fig 3.8 for lowest and highest carrier concentration InN/Sapphire thin films. These results suggest that our InN/Sapphire thin films are highly textured along c-axis, although polycrystalline in nature.

These rf sputtered InN/Sapphire films are highly degenerate and n-type in nature. The source of the n-type carriers in these films was investigated by determining the elemental composition using RBS. We used the InN/Sapphire thin films with highest carrier concentration, expecting largest stoichiometric deviation for this sample. The RBS data, shown in Fig 3.11(a), was acquired using a standard detector (angle of 140°), a 180° annular detector and a 40° annular detector using a $4\text{He}^+$ ions, 2 MeV beam from a Van de Graaff accelerator.

The In to N ratio for the sample was estimated by simulating the experimental results using a nuclear data function (NDF) simulation package [138]. The observed In:N ratio is 47:53, indicating excess nitrogen is present in these films. This excess nitrogen suggests that other compensating defects could be responsible for the excess charge carriers [2, 126]. This implies that samples prepared under nitrogen rich deposition conditions, which have lower carrier concentrations, may show more deviation in the In : N ratio, which suggests that acceptor-type defects such as In vacancies ($V_{\text{In}^{3-}}$) become more favourable. Thus excess nitrogen plays a minimal role in modifying the carrier concentration and the carriers are predominately donated by the interstitial oxygen present in these samples. The room temperature Raman spectra of the InN films having the lowest and highest carrier concentrations are shown in Fig 3.12(b). We observe the $E_2$ (low), $E_2$ (high), and $A_1$(LO) modes for InN at $\sim 90$, 490 and 580 $\text{cm}^{-1}$ respectively, consistent with the reported values [139]. The
Figure 3.12: (a) RBS spectra for highest carrier concentration InN/Sap thin film with a standard detector of 140° angle (red circle), 180° annular detector (blue square) and 30° annular detector (black triangle). The solid line is the NDF simulation fit to the experimental data. (b) Raman spectrum of the InN thin films having lowest carrier concentration (top panel) and highest carrier concentration (bottom panel). "*" indicates mode at 219 and 303 cm$^{-1}$ from In$_2$O$_3$. (c) Optical reflectance spectra of InN/Sap thin films (top panel) and absorption spectra (bottom panel). Closed (open) symbols and dotted (dashed) lines show the experimental data and simulated spectrum for the film having a carrier concentration of 1.26 × 10$^{21}$ cm$^{-3}$ (3.84 × 10$^{20}$ cm$^{-3}$) and (d) normalized plot of Im($-1/\epsilon(w)$) vs $w_p$ plot for different InN/Sap thin films, where the arrows indicate the corresponding $w_p$ values.
presence of additional peaks at $\sim 128, 305$ and $370 \text{ cm}^{-1}$, which are characteristics of bcc In$_2$O$_3$ [132, 140, 141, 136], argue the presence of In$_2$O$_3$ secondary phases, consistent with the observation of a finite oxygen content in these sample [132]. This excess oxygen in InN thin films is believed to be the main source for the excess carriers and highly degenerate nature of these films. Additionally this excess oxygen in these sputtered films may be sufficient to distort the InN lattice and break the local crystal symmetry. This can allow the excitation of the B$_1$ Raman mode, which is a silent mode in an ideal InN lattice. We noted the presence of the B$_1$(low) and B$_1$(high) modes at $\sim 200$ and $565 \text{ cm}^{-1}$ respectively, as shown in Fig 3.12(b). Some of the Raman active modes are absent in these highly disordered films, as shown in Fig 3.12(b)(bottom panel). The disorder present in the system cause lattice distortions, which results in the broadening of the Raman modes. In spite of lattice distortions, charge carriers can strongly interact with certain optical modes and influence their spectral characteristics. The suppression of the E$_2$(low) mode and broadening of the B$_1$(low), E$_2$(high) and A$_1$(LO) modes, as seen in Fig 3.12(bottom panel) shows the possible evidence of strong coupling between charge carriers and optical modes.

We have conducted optical and electronic studies of these InN films using UV-Vis-NIR spectroscopy and Hall effect measurement. The absorbance was calculated using the optical transmittance and reflectance and thus absorption coefficient ($\alpha$) was extracted. The reflectance and the absorption coefficient are plotted in Fig 3.12(c) for the InN thin films with the lowest and highest carrier concentrations. Most surprisingly, we observe two absorption peaks in contrast to the normal optical absorption spectrum of InN, where the typically optical response consists of direct bandgap absorption located at an energy corresponding to the bandgap energy plus the Moss-Burstein shift [122, 123]. The additional low energy absorption peak is attributed to the plasmon excitations in these highly degenerate InN films and is as strong as the direct bandgap absorption. The low energy absorption peak can be tailored by varying carrier concentration in InN thin films and it ranges from 0.45 to 0.8 eV for
samples with carrier concentration ranging from $3.84 \times 10^{20} \text{cm}^{-3}$ to $1.26 \times 10^{21} \text{cm}^{-3}$. There is a transparent region with a width of nearly $\sim 1$ eV between the plasmon and bandgap excitation region. This transparent window can be changed by changing the carrier concentration, as shown in the bottom panel of Fig 3.12(c) and thus allow these materials as a possible optical filters or similar other optoelectronic applications.

The optical reflectance for these films, shown in Fig 3.12(c), consist of a large reflection edge due to the plasmon excitation in the lower energy side of spectrum. The well defined interference fringes are seen on the high energy side because of interference between reflected waves from the surface and interface. This fringe width was used to calculate the thickness of the films using the known dielectric constant and is in good agreement with the thickness estimated from cross-sectional SEM micrographs. The reflection spectrum was simulated using the Drude model for the dielectric function [142, 143], where contributions form the LO-phonons and plasmon excitation are taken into account as:

$$\epsilon(\omega) = \epsilon_{\infty} \left[ 1 + \frac{\omega_{LO}^2}{\omega_{TO}^2 - \omega^2} - i \frac{\omega p^2}{\omega^2 + i \gamma} \right]$$

(3.1)

Here $\omega_{TO}/\gamma$ and $\omega_{LO}/\Gamma$ are the TO and LO phonon frequencies/damping respectively. $\omega_p = (4\pi N e^2/m^* \epsilon_0)$ is the plasmon frequency, $m^*$ is the electron effective mass and $\epsilon_0$ is the static dielectric constant. The phonon frequencies are determined using our Raman data and the damping factors are considered as variable parameters to simulate the reflectance spectra. In these films the plasmon energies are much larger than the LO-phonon energy so the coupling between the fundamental modes of plasmon and LO phonons is negligible. The estimated carrier concentrations of these InN films using the measured plasmon frequencies are consistent with the Hall effect measurements. Changing the carrier concentration by tailoring the deposition conditions results in a change in plasmon frequency together with a change in the optical absorption edge, as shown in the bottom panel of Fig 3.12(c). We also calculate the shift in the optical absorption edge beyond the true bandgap value $E_g$ for
samples having different electron density using Kane’s two-band K.p model [144]. This model takes into account the electron density dependent shift and the nonparabolic conduction band dispersion due to the small bandgap value for the absorption edge. The variation in the optical absorption is given as [144]

$$\bar{E}_g = E_g + \frac{\hbar^2 k_F^2}{2m_0} + \frac{1}{2} \left( E_g^2 + 4E_p \frac{\hbar v_F^2 k_F^2}{2m_0} \right)^{1/2} - E_g \frac{2e^2k_F}{\pi \epsilon_0} - \frac{e^2k_{TF}}{2\epsilon_0} \left[ 1 - \frac{4}{\pi} \tan^{-1} \left( \frac{k_F}{k_{TF}} \right) \right]$$

The last two terms in this equation take into account the renormalization of the bandgap energy due to electron-electron interaction effects. The terms $k_F = (2\pi 2N_e)^{1/3}$ and $K_{TF} = 2\sqrt{\pi}(k_F m^*/0.53\epsilon_0)$ are the Fermi and Thomas-Fermi wavevectors respectively. We have used electron density $N_e$, estimated from the plasmon resonance, $E_p$ is the energy parameter of the Kane’s two-band $k.p$ model, $E_g = 0.7$ eV and $E_p = 6.0$ eV to estimate the effective optical absorption edge. The calculated and measured values of $E_g$ for different carrier concentration InN samples are in good agreement. This suggests that optical absorption edge and plasmon frequency are both related to the carrier density of InN thin films.

The calculated resonance due to plasmon absorption resonance, $Im(-1/\epsilon(\omega))$ for these InN thin films with respect to plasmon frequency is shown in Fig 3.12(d). The plasmon resonance for these InN films lie in the infrared region (0.45-0.8 eV) of the electromagnetic spectrum. The half width of the Lorentzian line shape of the absorption peak provides a measure of the plasmon damping due to electron scattering from defects and lattice phonons. The variation in the widths of these peaks is consistent with the variation in sample disorder, as seen in the Raman spectra. The plasmon in the films with the highest carrier density is the most strongly damped. This plasmon resonance has absorption intensity similar to that of the direct bandgap absorption and can be thus useful for device applications in infrared region of electromagnetic spectrum. The plasmon energy can be tuned by varying carrier
concentration in the system without altering the stoichiometry. Additionally, these highly degenerated InN thin films could be useful as plasmon filters for thermophotovoltaic (TPV) systems. Detailed working principles of TPV devices are presented in reference [137]. In brief, TPV devices consists of two main components: the filtering layer and the absorption. The filtering layer reflects the spectral components with energy less than the bandgap energy of the absorption layer. The bandgap values of TPV systems range from $0.5 \leq E_g \leq 1.1 \text{ eV}$ [137]. Thus to enhance the performance and efficiency of the TPV device, the reflectance edge of the filter should match with the bandgap of absorption layer. These factors limit the carrier concentrations and optical mobilities of the optical filter in the range $10^{20} \leq N \leq 10^{21}\text{cm}^{-3}$ and $10 \leq \mu \leq 1000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively [137]. These highly degenerate InN thin films meet these conditions and can therefore filter out undesired incident signals by reflection and plasmon absorption, which may increase the efficiency of the devices.

We find that highly degenerate rf sputtered films may be suitable for various optical and electronic applications. The optical window with almost zero absorption between plasmon absorption and optical band edge can be used as an optical filter. The window of this optical filter can be tuned by changing the carrier concentration and thus plasmon frequency with in the same InN material. In these highly degenerate InN thin films the plasmon absorption is comparable to the bandgap absorption, suggesting the application of these InN thin films for electronic devices operating at IR energies. In addition the reflection and plasmon absorption in the infrared region can be used in TPV devices to avoid spurious signals to prevent unwanted heating.
3.2.5 PHONON MODES, $E_1$(LO) PHONON-PLASMON COUPLED MODES, AND CRITICAL POINTS IN INDIUM GALLIUM NITRIDE ($\text{In}_{1-x}\text{Ga}_x\text{N}$) THIN FILMS

The hexagonal wurtzite crystal structure of both, InN and GaN, as shown in Fig 3.2, allows the possibility of a homogeneous solid solution of $\text{In}_{1-x}\text{Ga}_x\text{N}$ for $0 \leq x \leq 1$, as depicted in Fig 3.1. This offers the possibility of engineering bandgap ranging from near short wavelength infrared (0.7eV) to ultraviolet (3.4eV) region of electromagnetic spectrum. The wavelength emitted from light emitting diodes depends on the bandgap of the active layer [14], which can be controlled by controlling the InN/GaN ratio in the $\text{In}_{1-x}\text{Ga}_x\text{N}$ compound. $\text{In}_{1-x}\text{Ga}_x\text{N}$ compounds are also radiation resistant materials and suitable for multijunction tandem solar cells which are useful for satellite applications [22]. As mentioned earlier, the growth of p-type $\text{In}_{1-x}\text{Ga}_x\text{N}$ at lower bandgap side i.e. lower value of x, is still very challenging and surface electron accumulation in the $\text{In}_{1-x}\text{Ga}_x\text{N}$ compound near the surface poses another problem hiding p-type conductivity in the acceptor doped bulk compounds [117, 19, 118].

Thus knowing that $\text{In}_{1-x}\text{Ga}_x\text{N}$ semiconductors have great potential in electronic and optical devices operating in the near-infrared (NIR) region, it is important to investigate the phonons spectra of these materials in the NIR range. The lattice vibrations play a dominant role in the optical properties of materials.

In this section, we will discuss $E_1$(LO) phonon-plasmon coupled modes using IR reflectance spectra and the critical points in the band structure for $\text{In}_{1-x}\text{Ga}_x\text{N}$ system, using UV-Vis-NIR reflectance spectra. Also we will discuss about the effects of source excitation energy on the scattering efficiency of various Raman modes and variations in their energies with increasing Ga atomic fraction in the InN compound matrix.

$\text{In}_{1-x}\text{Ga}_x\text{N}$ thin film with $x = 0, 0.15, 0.30$ and $0.54$ were prepared by molecular beam epitaxy (MBE), discussed in section 3.2.1. The thickness of these films is $\sim 0.6\mu\text{m}$. The
Figure 3.13: (a) IR reflectance spectra of In$_{1-x}$Ga$_x$N ($x = 0, 0.15, 0.30$ and $0.54$) thin films under normal incidence. The dashed curves are the corresponding theoretical simulated reflectance curves. (b) variation of critical point energies of In$_{1-x}$Ga$_x$N samples as a function of $x$. The solid lines show the fitted data.

physical properties such as carrier concentrations and Hall mobilities of these thin films were determined using Van der Pauw method at room temperature and their values are listed in Table (1) of reference [145]. We noticed the increase in carrier concentration and decrease in mobility with increasing Ga atomic fraction in the InN matrix. The infrared (IR) spectra were obtained at normal incident configuration for $x=0, 0.15, 0.30$ and $0.54$ In$_{1-x}$Ga$_x$N thin films and are plotted in Fig 3.13(a). The sapphire IR reflectance spectrum is shown in top panel of Fig 3.13(a). Due to small thickness of In$_{1-x}$Ga$_x$N layer compared to the sapphire, a significant fraction of the light reaches the sapphire surface and is reflected back. When incident energy in reflectance measurements is less than the bandgap energy of In$_{1-x}$Ga$_x$N, we observe many sharp reflectance edges due to low energy phonons reflection from the sapphire and film layers as shown in Fig 3.13(a). The dominance of the reflectance from sapphire is clearly observed in the reflectance spectra of all the samples in the lower energy
range. The lowest panel shows the infrared reflectance for pure InN film. The overall profile of the reflectance spectrum for wavevectors less than $600 \text{ cm}^{-1}$ and some of the prominent reflection dips at $390 \text{ cm}^{-1}$ and $630 \text{ cm}^{-1}$ can be trivially associated with the reflectance from the sapphire infrared phonon modes. The plasmon energy for the InN film is very close to $E_1(\text{LO})$ phonon mode, so we expect the strong plasmon-phonon coupling in these thin films should influence strongly the overall reflectance. We have calculated the reflectance due to plasmon-$E_1(\text{LO})$ phonon using a dielectric function

$$\varepsilon(\omega) = \varepsilon_\infty \frac{(\omega^2 - \omega_+^2 + i\gamma_+ \omega)(\omega^2 - \omega_-^2 + i\gamma_- \omega)}{(\omega^2 + i\gamma_P \omega)(\omega^2 - \omega_{\text{TO}}^2 + i\gamma_{\text{TO}} \omega)}$$

(3.3)

Here $\omega_i/\gamma_i (i = +, -, \text{and} P)$ are the energies/damping constants for the coupled modes, $E_1(\text{TO})$ phonon and plasmon modes respectively. The transverse optic (TO) mode frequency was calculated using Lyddane-Sachs-Teller relation $\omega_{\text{TO}} = \omega_{\text{LO}} \sqrt{\varepsilon_\infty / \varepsilon_0}$, where $\varepsilon_0$ is the static and $\varepsilon_\infty$ is the dynamical dielectric constant of the InN film. The energies of the lower ($\omega_-$) and higher ($\omega_+$) coupled modes are calculated using the following relation

$$\omega_+ = \sqrt{0.5 \left[ \omega_p^2 + \omega_{\text{LO}}^2 \pm \sqrt{\left( \omega_p^2 + \omega_{\text{LO}}^2 \right)^2 - 4 \omega_p^2 \omega_{\text{TO}}^2} \right]}^{1/2}.$$  

(3.4)

The plasmon frequency $\omega_p = N e^2 / \varepsilon_\infty m_e^*$ is estimated from the electron density $N_e$ and the corresponding effective mass $m_e^*$. There are two main inputs in the above equations which are $E_1(\text{LO})$ phonon energy and plasmon energy $\omega_p$. For the calculations of $\varepsilon(\omega)$ for InN film, we have taken $E_1(\text{LO})=600 \text{ cm}^{-1}$ and for $\omega_p$, we took $\varepsilon_\infty$ and density dependent $m_e^*$ values. The simulated reflectance including the plasmon and phonon interactions is shown as a dotted line (red in colour) in Fig 3.13(a). The energies of the lower and higher energy coupled modes, for a defects free system, are $360 \text{ cm}^{-1}$ and $725 \text{ cm}^{-1}$ respectively. Thus in a defect free InN system we would expect reflectance edges at these energies; however presence of defects can smear out these edges. Due to the presence of charged defects, plasmon is
relatively more damped than the phonons in these films. The damping plasmon has stronger influence on the spectral features of the lower energy coupled mode than that of the higher energy coupled mode. As result, the reflectance for wavevectors less than 400 \( cm^{-1} \), the features are dominated by the sapphire. However, for wave vectors ranging from 600 \( cm^{-1} \) to 800 \( cm^{-1} \), the over all fall of the reflectance spectrum is very similar to the calculated plasmon-E\(_1\)(LO) phonon reflectance. On the contrary, the reflectance due to the sapphire is almost constant in that regime, suggesting the strong coupling of the E\(_1\)(LO) phonon with the plasmon in these films. As the value of \( x \) is varied in In\(_{1-x}\)Ga\(_x\)N films, the behavior of the reflectance for wave vectors in the range from 600 \( cm^{-1} \) to 800 \( cm^{-1} \) remains almost the same for all the films. This is consistent with the fact that the values of carrier density are almost same for all the In\(_{1-x}\)Ga\(_x\)N films. Reflectance behavior for other In\(_{1-x}\)Ga\(_x\)N films is very similar to the InN films, except the dip at 445 \( cm^{-1} \) observed in InN films moves toward higher wavevectors. This dip has been associated with E\(_1\)(TO) mode of the In\(_{1-x}\)Ga\(_x\)N films.

We have carried out UV-Vis-NIR reflectance spectrum from 175 to 3300 nm spectral range and utilized to study its band structure. The characteristics structures, like peaks and shoulders in a reflectance spectrum, are related to the optical transitions at the critical points of the energy difference between the initial and final energy bands involved. They are defined by the relation:

\[
\nabla_k [E_c(k) - E_v(k)] = 0
\]

for some values of wavevector \( k \). So a reflectance spectrum may contain series of critical points in the total joint density of states. Normally, critical points are studied using ultraviolet-vacuum ultraviolet (UV-VUV) reflection spectrum between 4 and 20 eV range using the synchrotron radiation [146]. However, we observed these critical points in our high energy reflection data and are summarized in Fig 3.13(b) for different Ga atomic fraction in In\(_{1-x}\)Ga\(_x\)N samples. Recently about 7 critical point transitions have been observed for InN in the synchrotron VUV reflection spectrum between 4 and 20 eV energy range [146]. In our
reflectance measurements over a limited energy range from 4.0eV to 7.0eV, we observed two main transition structures known as A and B. In the structure A, two very well defined peaks with energies 4.75eV, 5.36eV are observed. In the structure B, at least one critical point at 6.12eV was observed. These energies agree very well with the empirical pseudopotential method calculations [147] and ellipsometric measurements [148] on InN films. As the Ga content is increased in In$_{1-x}$Ga$_x$N alloys, these critical points shift towards higher energies, as shown in Fig 3.13(b). We also calculated the variation of these critical point energies using the relation [20]

$$E_g(x) = E_g(GaN)x + E_g(InN)(1 - x) - bx(1 - x)$$

(3.6)

where $E_g(GaN)=3.42eV$, $E_g(InN)=0.77eV$ and bowing factor $b=1.43eV$ for the In$_{1-x}$Ga$_x$N system, and are shown with solid lines in Fig 3.13(b). The lowest curve in Fig 3.13(b) shows the variation in the direct bandgap for different In$_{1-x}$Ga$_x$N thin films. These variation are in good agreement with the observed experimental values.

One of the interesting consequences of the strong electron-phonon Fröhlich interaction in wurtzite crystals is a large enhancement of light scattering by polar LO phonons when the energy of the incident photon is close to the band gap energy of the semiconductor. In many cases it has also led to the excitation of replica phonon modes. There are six Raman active modes in wurtzite In$_{1-x}$Ga$_x$N structure, which are $E_2$(low), $E_2$(high), $A_1$(TO), $A_1$(LO), $E_1$(TO), and $E_1$(LO) modes. These modes are observed in the first order Raman spectrum of In$_{1-x}$Ga$_x$N system. Other optical modes $B_1$(low) and $B_1$(high) are silent in wurtzite nitrides but are occasionally observed in disordered films [132]. We investigated the influence of excitation energy on the Raman intensity of these modes by choosing two laser energies—the green laser (514.5nm=2.41eV) having energy larger than the bandgap energy of In$_{1-x}$Ga$_x$N films we have studied and the red (830nm=1.5eV) laser having energy between the bandgap energy of $x=0.3$ film ($E_g=1.30$ eV) and of $x=0.54$ film ($E_g=1.85$ eV). Out of the the six
Raman active modes, we observe $E_2$(low), $E_2$(high) and $A_1$(LO) first order Raman modes only, when the samples are excited by red laser(Fig 3.14(a)).

It is interesting to note that $E_2$(High) mode and $A_1$(LO) modes are have nearly same intensity for InN film (Fig 3.14(a) lowest panel). Replica mode ($2A_1$(LO)) of $A_1$(LO) is observed in all In$_{1-x}$Ga$_x$N films. In between $E_2$(High) and $A_1$(LO) modes, one can also observe a mode at $\sim 540\text{cm}^{-1}$ which is not seen with green laser (Fig 3.14(b)) because of the stronger absorption of the laser energy by the InN layer. This mode is observed for all our In$_{1-x}$Ga$_x$N films. A similar mode has been observed [149] in post annealed InN thin films and is marked as an unidentified feature. We associate this mode with $A_1$(TO) of GaN originating from the GaN buffer layer used in all the films. As Ga atomic fraction in In$_{1-x}$Ga$_x$N is increased, the energies of these modes ($E_2$(High), $A_1$(LO), and $2A_1$(LO)) increases, as expected. However there is a dramatic decrease in the intensity of $E_2$(high) mode relative to $A_1$(LO) mode and it also more damped due to the lattice disorder. At $x = 0.54$ $E_2$ mode has almost disappeared into the noise signals. Variation in the energies of these modes is shown in Fig 3.14(c). The observed variation deviates slightly from linearity with the increasing Ga atomic fraction. With increasing $x$ value, the absorption of the laser energy decreases in the In$_{1-x}$Ga$_x$N layer of the films and at $x=0.54$, the bandgap value ($E_g = 1.86 \text{eV}$) of In$_{1-x}$Ga$_x$N layer becomes larger than the laser energy. This leads to a stronger transmission of laser energy into the subsequent layers-GaN buffer and Sapphire substrate layers and as a result intense excitations of many sapphire modes as marked by * in the figure is observed (Fig 3.14(a) top panel, $x=0.54$).

A big change in Raman intensities of these modes, compared to red laser excitation, is observed when the samples are excited with green laser (Fig 3.14(b)). The green laser energy is much larger than the bandgap energies of the In$_{1-x}$Ga$_x$N layer of the films, so there is a very little transmission of the laser energy into the GaN and sapphire layers and as result no sapphire and GaN modes are observed in Fig 3.13(b). With increasing values of
Figure 3.14: Raman spectra of In$_{1-x}$Ga$_x$N ($x = 0$, 0.15, 0.30 and 0.54) thin films using (a) red laser (1.58 eV) excitation source, (b) green laser (2.41 eV) excitation source. The dashed lines represent the variation of $E_2$(low), $A_1$(LO) and its replica $2A_1$(LO) mode energy variation with increasing Ga atomic fraction. (c) the energy variation of $1A_1$(LO), $2A_1$(LO), $E_2$(low) and $E_2$(high) modes with respect to Ga atomic fraction and (d) energy variation in the ration of $A_1$(LO)/$E_2$(high) with respect to the Ga atomic fraction for In$_{1-x}$Ga$_x$N thin films.
x, bandgap energy of In$_{1-x}$Ga$_x$N layer comes closer to the laser energy leading to a stronger scattering from the longitudinal optical phonons (A$_1$(LO) and 2A$_1$(LO)) as expected from the electronic resonance effects. At x=0.54, the A$_1$(LO) and 2A$_1$(LO) phonons become quite intense compared to other E$_2$ modes. The Raman intensities of E$_2$(low) and E$_2$ (high) modes decrease with increasing values of x and at x=0.54, these modes cease to exist due to overdamping. We could not observe E$_2$(low) mode when samples are excited with red laser. As with red laser, the energies of these modes increase linearly with increasing concentration of Ga atoms. At a particular value of x, there is no change in the frequency of these modes when energy of the laser is changed.

Thus, using low energy reflectance measurements we have observed excitation of E$_1$(LO) mode and its coupling with plasmon whose energy values for these films are close to the energy of E$_1$(LO) phonon. In the higher energy reflectance from 4.0eV to 7.0eV, very well resolved critical points of the band structure are seen. We also investigated the influence of excitation source frequency, using green and red lasers, on the intensity of various Raman modes and found that the A$_1$(LO) mode become very intense for the films whose bandgap value approaches the laser energy and similarly we found that the intensities of E$_2$ modes(low and high) are also sensitive to the excitation frequency used in Raman spectroscopy.

### 3.2.6 ROOM TEMPERATURE MAGNETIC PROPERTIES AND SPIN POLARIZATION IN In$_{1-x}$Cr$_x$N THIN FILMS

The III-nitride semiconductors are widely used in optoelectronic and photovoltaic applications because of their excellent electronic properties. Few magnetic studies on III-V and especially III-nitrides are found in the literature. Oxide based DMSs such as TiO$_2$, In$_2$O$_3$ and ZnO are much more extensively studied [36], although the origin of magnetism is still controversial in these systems [36, 37]. Ohno and Munekata’s work on Mn doped InAs opened up the possibility of III-V compounds as potential hosts for dilute magnetic
Figure 3.15: Curie temperature for various III-V semiconductor compounds, containing 5% Mn per cation in 2+ charge state and $3.5 \times 10^{20}$ holes cm$^{-3}$. [23]

The search for new semiconductors with better magnetic properties is an ongoing process and challenge for many spintronic applications.

The theoretical work by T. Dietl accelerated the III-nitride dilute magnetic semiconductor research [150, 23]. The Curie temperature ($T_C$) of various dilute magnetic semiconductors, calculated using mean field theory is shown in Fig 3.15.

The $T_C$ for these systems was theoretically modeled for an Mn doped, hole mediated ferromagnetism in highly degenerate p-type systems. These studies suggest III-nitrides such as GaN and InN and II-VI Oxides such as ZnO, are possible DMS, which can ferromagnetism above room temperature. Studies on III-nitride based DMS are focused on Mn and Cr doped GaN and AlN [151, 152, 153] and there are few reports on magnetic study of the transition element doped InN system [154, 155, 156]. InN exhibits a small spin orbit coupling of $\sim$3 meV, which allows longer spin lifetimes because of lower spin-orbit scattering. This should be compared to GaAs, which has a spin orbit coupling of 0.34 eV [157]. Additionally, the
high carrier mobility and carrier drift velocity make InN a better material for many device applications.

The synthesis and structural investigation of \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N}/\text{Sap} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N}/\text{Sap} \) thin films are discussed in sections 3.2.1 and 3.2.2. The XRD analysis does not show any conventional magnetic impurities such as Cr clustering, or any \( \text{Cr}_2\text{O}_3 \) phase. However, XRD alone may not be able to identify small amount of impurities. We carried out room temperature \( \mu \)-Raman studies on these sample using 514.5nm green laser as an incident light, to probe any magnetic or other impurities present in these thin films. The observed Raman spectrum for both the samples are shown in Fig 3.16 (c).

The expected \( E_{2}\text{(high)} \) and \( A_1\text{(LO)} \) modes for both \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) thin films are observed at 490 and 580 \( cm^{-1} \) respectively. The broadness of these modes is consistent with the polycrystalline nature of these samples, as shown in Fig 3.16 (c) and indicate the presence of various defects in the system. Additional peaks observed at 128 and 305 \( cm^{-1} \) (marked with *) in the Raman spectrum are the characteristics of bcc-structured \( \text{In}_2\text{O}_3 \) vibrational Raman modes [132]. This suggests the presence of oxygen in the InN system and the observed \( \text{In}_2\text{O}_3 \) may be present in the grain boundaries or even inside the grains, consistent with our previous observations. This additional oxygen is sufficient to distort the regular InN lattice and my result into the activation of \( B_1 \) silent mode of InN crystal lattice due to the possible violation of the Raman selection rules in these thin films. We believe that additional mode near 200 \( cm^{-1} \) is disorder activated \( B_1 \) mode for InN crystal lattice. Apart from \( \text{In}_2\text{O}_3 \) impurities in these films, we did not find any conventional magnetic impurities.

We carried out the optical characterization of these thin films using UV-Vis-NIR spectroscopy. We measured the optical transmittance and reflectance in the range from 175 to 3300 nm. The interference fringes from the reflectance spectrum of these films were used to calculate the thickness of these films and thickness is \( \sim 1\mu m \) for both films. The absorp-
Figure 3.16: \(((\alpha \times E)^2)\) versus energy for (a) \(\text{In}_{0.98}\text{Cr}_{0.02}\)N and (b) \(\text{In}_{0.95}\text{Cr}_{0.05}\)N thin films. The red line is an extrapolation to the linear region for optical absorption edge and the lower energy peak \(\sim 0.7\) eV is the plasmon absorption peak for both the films. (c) Raman spectrum for \(\text{In}_{0.98}\text{Cr}_{0.02}\)N (bottom panel) and \(\text{In}_{0.95}\text{Cr}_{0.05}\)N (top panel) thin films where \("*\) corresponds to the peaks from the 128 and 305 cm\(^{-1}\) modes from \(\text{In}_2\text{O}_3\) and (d) the temperature dependence resistivity for \(\text{In}_{0.98}\text{Cr}_{0.02}\)N and \(\text{In}_{0.95}\text{Cr}_{0.05}\)N thin films.
The optical absorption edge was estimated by extrapolating the linear portion of \((\alpha \ast E)^2\) to \(E = 0\). The optical band edge for both films is \(\sim 1.8\) eV, consistent with that observed for highly degenerate InN thin films [132]. The room temperature photoluminescence (PL) was carried out using a 514.5 nm wavelength excitation source and the PL spectra are shown in Fig 3.17. The extracted PL peaks are in good agreement with the observed optical absorption edge for these thin films.

In addition to the direct bandgap absorption there is an additional absorption at lower energies \(\sim 0.7\) eV for both \(\text{In}_{0.98}\text{Cr}_{0.02}\text{N}\) and \(\text{In}_{0.95}\text{Cr}_{0.05}\text{N}\) thin films. This absorption is attributed to collective plasmon excitations, due to the highly degenerate n-type behaviour of these thin films and is comparable to the direct bandgap absorption observed in these thin films. This observed plasmon frequency was used to calculate carrier concentrations in these samples using equation \(\omega_p = 4\pi N_e e^2/m^*\epsilon_0\), where \(\omega_p\) is the plasmon frequency, \(m^*\) is
the electron effective mass and \( \epsilon_0 \) is the static dielectric constant. Thus calculated carrier concentrations using the respective plasmon frequency for \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \)

thin films are \( 6.7 \times 10^{20} \) and \( 7.2 \times 10^{20} \text{cm}^{-3} \) respectively and are in good agreement with the room temperature Hall effect measurement values. We carried out temperature dependent electrical resistivity measurements for these thin films from 10 K to 300K, using Quantum Design PPMS (Physical Properties Measurement System), as shown in Fig 3.16 (d). These films show the metallic resistivity over the entire temperature range and is almost constant, indicating that carrier concentrations are relatively insensitive to temperature.

In order to understand the magnetic behaviour of these \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) films, we carried out in-plane temperature and field dependent magnetic measurements using a Quantum Design SQUID (Superconducting QUantum Interference Devices) magnetometer. The temperature dependent magnetization plots for \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) are shown in Fig 3.18 (a) and (c) respectively. These measurements were carried out under zero field cooled (ZFC) and field cooled (FC) conditions at 500 Oe. The magnetization for both samples exhibit similar temperature dependence and we observe a considerable increase in magnetization below 50 K, which we associate to a Curie tail rise from the paramagnetic contributions of the Cr ions in the sample. These temperature dependent magnetization measurement also confirms the absence of any Cr cluster type impurities as we do not observe the splitting between ZFC and FC magnetization curves Fig 3.18 (a) and (c) for 2% and 5% Cr doped InN thin film samples.

The room temperature field dependent magnetization curves for both \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) are shown in Fig 3.18 (b) and (d) respectively. These data have been corrected for the small diamagnetic contribution from the sapphire substrate, with the inset showing the M(H) data without any correction. These measurements clearly indicate that both films exhibit room temperature ferromagnetic ordering with saturation magnetizations of 0.15 and 0.30 emu cm\(^{-3}\) for \( \text{In}_{0.98}\text{Cr}_{0.02}\text{N} \) and \( \text{In}_{0.95}\text{Cr}_{0.05}\text{N} \) respectively. We have also carried out field
Figure 3.18: (a) Temperature dependent magnetization for an $\text{In}_{0.95}\text{Cr}_{0.05}\text{N}$ thin film. (b) Field dependent magnetization at 15 K (red triangles) and 300 K (black circles) for an $\text{In}_{0.95}\text{Cr}_{0.05}\text{N}/\text{Sap}$ thin film. (c) Temperature dependent magnetization for an $\text{In}_{0.98}\text{Cr}_{0.02}\text{N}$ thin film and (d) field dependent magnetization at 15 K (red triangles) and 300 K (black circles) for an $\text{In}_{0.98}\text{Cr}_{0.02}\text{N}/\text{Sap}$ thin films. The substrate background was subtracted for both samples and the respective unprocessed data is shown in the inset.
dependent magnetization studies at 15K, as shown in Fig 3.18 (b) and (d) with red triangular symbols and observed that the saturation magnetization for both films are very similar to their room temperature behaviour. This suggests that the ferromagnetic behaviour of these samples is intrinsic and is not associated with any Cr nano-clustering or secondary magnetic impurities in these samples. We believe that the intrinsic ferromagnetic ordering in these samples is electron carrier mediated, an analog of hole mediated ferromagnetism in GaMnAs [33] and associate the temperature insensitive saturation magnetization in these samples to the observed carrier concentration, which is approximately temperature independent over this range.

To further extend our understanding of magnetism and spin-charge coupling in these samples, we carried out direct measurements of electron spin polarization using Point Contact Andreev Reflection (PCAR) spectroscopy [158, 159]. This technique is based on the sensitivity of the process of quasiparticle conversion into the Cooper pairs (Andreev reflection) at superconductor/normal metal contact to the degree of spin imbalance at the Fermi level. This technique can be used to measure the spin polarization of the charge carriers in dilute magnetic semiconductors, where the conductance is measured across a ferromagnet/superconductor interface. The electrical transport at energies below superconducting gap across the ferromagnet/superconductor interface depends on the process of quasiparticle conversion into Cooper pairs as the current propagates across the interface, which requires the electrons with spin up and down both and hence, is limited by the minority spin population in a ferromagnet. The conductance curves are obtained in a point contact geometry with a Nb superconducting tip. The conductance curves for In$_{0.98}$Cr$_{0.02}$N/Nb and In$_{0.95}$Cr$_{0.05}$N/Nb thin films are shown in Fig 3.19 (a) and (b) respectively.

These PCAR measurements were carried out at 1.7 K. We observed that these conductance curves show a characteristic dip at zero bias voltage indicating the suppression of Andreev reflection. These experimental conductance curves were simulated using a theo-
Figure 3.19: Normalized conductance curves for superconducting Nb contacts with (a) In$_{0.98}$Cr$_{0.02}$N and (b) In$_{0.95}$Cr$_{0.05}$N thin films. The solid red lines show simulated fits to the experimental data obtained using the diffusive model.

retical model proposed by Mazin et al [160, 161], to estimate the electrical transport spin polarization, $P$ and the interfacial barrier strength $Z$. The interface barrier strength $Z$ for these samples is quite low $\sim 0.4$ and these is no strong dependence of spin polarization on $Z$. This analysis averaged over a number of different point contacts in numerous samples, gives a spin polarization of $40\% \pm 5\%$ for both samples with in the experimental error limits. This strong spin polarization observed in both In$_{0.98}$Cr$_{0.02}$N and In$_{0.95}$Cr$_{0.05}$N thin films suggest the possibility of strong coupling between ferromagnetic moment and the charge carriers.

Thus we demonstrated that rf sputtered In$_{0.98}$Cr$_{0.02}$N and In$_{0.95}$Cr$_{0.05}$N thin films ferromagnetism above room temperature, which is nearly temperature independent. Spin polarization measurements on these samples strongly suggest a correlation between ferromagnetism and electron carrier concentrations.

3.3 CONCLUSION

We have investigated the fabrication of InN, In$_{1-x}$Ga$_x$N and In$_{1-x}$Cr$_x$N films and carried out extensive structural/microstructural, optical, electrical, and magnetoelectronic studies. InN shows a strong propensity to develop highly degenerate n-type behaviour. The main
source of this degeneracy is the excess oxygen and/or hydrogen present as defects in the InN matrix. We have investigated the effect of excess oxygen in the InN host matrix using an In$_2$O$_3$ target to incorporate excess oxygen, which was compared to a InN sample prepared using a high purity In metal target. Our elemental XPS and optical ($\mu$-Raman and UV-Vis-NIR spectroscopic) and electrical measurement suggest that an initial incorporation of oxygen into the InN host matrix forms point defects, acting as electron donors into the system. However after a certain oxygen concentration, the carrier concentration is saturated as excess oxygen begins to form In$_2$O$_3$ clusters. Additionally, we investigated the strong plasmon absorption in these highly degenerate rf sputtered InN thin films. This plasmon frequency can be tuned by varying the carrier concentration into the InN system. We were able to tune plamon frequency from 0.45 eV to 0.8 eV by changing the carrier concentration from $3.84 \times 10^{20}$ to $1.26 \times 10^{21}cm^{-3}$. The plasmon absorption intensity is comparable to the direct bandgap absorption suggesting possible applications for IR electronic device applications and plasmon filter for thermophotovoltaic devices. Additionally we observe a window of $\sim 1$ eV between the plasmon absorption and optical absorption edge, suggesting applications for optical filters. Our IR reflection studies for In$_{1-x}$Ga$_x$N system show strong $E_1$(LO) phonon-plasmon coupling. We used high energy UV-Vis-NIR reflection studies to identify critical point energies for In$_{1-x}$Ga$_x$N and the observed values are in agreement with the theoretically estimated and previously reported results. We also studied the magnetic properties of Cr doped InN. Our observations suggest that In$_{1-x}$Cr$_x$N exhibit ferromagnetism above room temperature and a finite spin polarization of $\sim 40\%$ for 2% and 5% Cr doped InN thin films.
Chapter 4

INDIUM OXIDE COMPOUND SEMICONDUCTOR - OPTICAL, ELECTRONIC AND MAGNETIC PROPERTIES

4.1 INTRODUCTION

Indium oxide (In$_2$O$_3$) is an interesting group III oxide (AlIIH$_2$O$_3$ where A = Al, Ga and In) compound semiconductor. It has a cubic bixbyite crystal structure and space group Ia$\bar{3}$ ($T_h^7$) with lattice constant $a=10.118\,\text{Å}$, as shown in Fig 4.1, under ambient conditions [162]. One unit cell of In$_2$O$_3$ consists of 16 units of In$_2$O$_3$. Thus a defect free indium oxide consists of 80 atoms in one unit cell.

Two non-equivalent indium cation sites are present in the indium oxide crystal and occupy Wycoff positions 8b and 24d, while anion oxygen atoms occupy Wyckoff positions 48e, as shown in Fig 4.1(b). In Fig 4.1(b), the separation between indium and oxygen atoms is
Figure 4.1: (a) In$_2$O$_3$ cubic bixbyite crystal structure and (b) non equivalent b and d In cation sites and O vacancies in In$_2$O$_3$. 

(a)

(b)

48 anions e positions

16 anions vacancy

8 cations b-positions

24 cations d-positions

In(1)

In(2)
2.18 Å and oxygen atoms are situated at the corners of the cube with two body-diagonally opposite corners unoccupied. In Fig 4.1(b), the In-O separations are 2.13, 2.19 and 2.23 Å, where the oxygen atoms occupy positions at the corner of the cube with two face-diagonally opposite corners unoccupied. Thus both indium sites can be viewed as an incomplete body centered cubic structure with an indium atom located at the center and oxygen atoms at the corners with one fourth of the anions missing [162].

This material exhibits high electrical conductivity and high optical transparency [24] and thus, is an important transparent electronic material. This is widely used in the form of tin doped indium oxide in light emitting diodes (LEDs), liquid crystal displays (LCDs), electro-optic devices, antireflection and antistatic coatings, gas sensors, transparent electrodes for various display devices and transparent contacts [24]. Recent studies by Panguluri et al [28] have shown that oxygen deficient and highly conducting In$_2$O$_3$ thin films are ferromagnetic above room temperature and show $\sim 55\%$ spin polarization. This makes In$_2$O$_3$ a promising candidate for magneto-optic and spintronic applications. However, despite these potential applications, some fundamental properties of In$_2$O$_3$ remain controversial. Most significantly, the nature of the band gap is still under intense debate. Earlier studies of the optical absorption edge found a direct band gap of $\sim 3.7$ eV with an onset of indirect phonon assisted transitions starting at $\sim 2.6$ eV [163]. More recent theoretical [164] and X-ray photoelectron spectroscopy studies [165] showed that the band edge transitions in In$_2$O$_3$ are forbidden because of the even parity for states at both the top of valence band and the bottom of conduction band. These studies suggest a strong optical transition from 0.8 eV below the top of the valence band to the conduction band. Taken together with recent optical measurements on high quality epitaxial In$_2$O$_3$ thin films [166], these references suggest a lower intrinsic direct band gap of $\sim 2.6$ eV in contrast to the previously accepted value of $\sim 3.7$ eV.

In this section we will investigate the optical and electronic properties of rf sputtered In$_2$O$_3$ thin films and discuss in detail the observed room temperature persistent photocon-
ductivity (PPC), stable transparent conducting oxide nature of undoped oxygen deficient In$_2$O$_3$ thin films, and the onset of strong plasmon absorption behaviour and their switchability using thermal treatment of In$_2$O$_3$ thin films.

4.2 EXPERIMENTS AND RESULTS

4.2.1 FABRICATION OF INDIUM OXIDE (In$_2$O$_3$) THIN FILMS

The In$_2$O$_3$ thin films were fabricated on c-axis (0001) sapphire and highly conducting n-type (100) silicon substrates by radio frequency (rf) (13.56 MHz) magnetron sputtering system using a high purity (5N) indium metal target. The sputtering chamber was maintained at the base pressure of $10^{-6}$ torr using cryo-pump for more than 12 hours to remove any possible residual gaseous impurities before deposition. These thin films were grown at $T = 475\pm 5$ °C with a forward RF power of 100 W for 2 hours to get the desired thickness of $\sim 1\ \mu$m for most of the films. The total working pressure of the sputtering chamber was kept constant at $1.5 \times 10^{-2}$ torr for most of the film deposition, with an admixture of high purity oxygen as a reactive gas at $\sim 1.5 \times 10^{-3}$ torr pressure and remaining high purity argon ($\sim 1.35 \times 10^{-2}$ torr) as the sputtering gas respectively. These as-prepared In$_2$O$_3$ thin films are highly insulating and were annealed at 600 °C for 9 hours under high vacuum, on the order of $\leq 10^{-6}$ torr, to understand the effects of oxygen vacancies and their role on the optical and electronic properties of this system. We have conducted a detailed structural, optical, electronic and magnetic characterization of both as prepared (AP) and vacuum annealed (VA) In$_2$O$_3$ thin films.
4.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF In$_2$O$_3$ THIN FILMS

The extensive structural and microstructural characterization of the as prepared (AP) and vacuum annealed (VA) In$_2$O$_3$ thin films was carried out using X-ray diffraction (XRD), cross-sectional scanning electron microscope (SEM), transmission electron microscope (TEM), and $\mu$-Raman. A representative XRD pattern for as prepared (AP) and vacuum annealed (VA) In$_2$O$_3$ thin films on sapphire substrate is shown in Fig 4.2.

The XRD pattern can be fully indexed to the cubic bixbyite In$_2$O$_3$ structure, consistent with the polycrystalline nature of these films. The intense XRD peaks at $2\theta$=30.86$^0$ and 63.86$^0$ in Fig 4.2, correspond to the (222) and (444) reflections, indicating the films are highly textured along the (222) orientation. The semi-log plots of these XRD patterns are shown.
Figure 4.3: (a) Cross-sectional SEM of an as grown In$_2$O$_3$ film on a silicon substrate and (b) HRTEM image of an In$_2$O$_3$ film with misfit or edge dislocations, marked by arrows. Inset: Fast Fourier transform of the image indicating the fourfold symmetry of In$_2$O$_3$

as inset, demonstrating the polycrystalline nature of In$_2$O$_3$ thin films. The cross-sectional SEM micrograph is shown in Fig 4.3(a), indicating the presence of 1µm long 50 nm wide columnar grains of In$_2$O$_3$ along the (222) direction.

A high-resolution transmission electron microscopy (HRTEM) image of the film is shown in Fig 4.3(b), taken along [100]. The electron diffraction pattern, shown in inset, clearly indicates the four fold symmetry with a spacing of 2.5 Angstrom corresponding to the (400) hkl planes. In addition, the microstructural characterization of these In$_2$O$_3$ thin films was carried out using $\mu$-Raman spectroscopy to investigate the possible Raman active modes in the system and thus, the crystalline quality. The room temperature Raman spectrum was collected on these films using 514.5 nm green laser as the excitation source. The represen-
Figure 4.4: Room temperature Raman spectra for In$_2$O$_3$ thin films on (100) MgO, (1102) r-axis Al$_2$O$_3$, (0001) c-axis Al$_2$O$_3$ substrates and In$_2$O$_3$ bulk powder sample, from bottom to top panel respectively. The corresponding Raman spectra for different substrates are shown with red curves in the respective panels.

A representative room temperature Raman spectrum of In$_2$O$_3$ thin films and bulk powder sample is shown in Fig 4.4.

The indium oxide bixbyite cubic lattice belongs to the space group Ia$\bar{3}$ ($T_h^7$) with 16 molecules per unit cell. The 32 indium atoms fit into the special primitive cell, which contains only 8 molecular units and thus gives rise to the a total number of 120 phonon branch [167]. The factor group analysis at the center of the Brillouin zone i.e. Γ point yields the following irreducible representation of the optical phonon normal modes:

$$\Gamma = 4A_g + 4E_g + 14F_g + 5A_u + 5E_u + 16F_u$$ (4.1)

Here $A_g$, $E_g$ and $F_g$ modes are Raman active modes, the $A_u$ and $E_u$ modes are silent modes and the $F_u$ modes are infrared (IR) active modes. Thus group theoretical analysis predicts 22 possible Raman active modes. The Raman spectrum was collected for In$_2$O$_3$
thin films on different substrates as shown in Fig 4.4, together with the bulk In$_2$O$_3$ powder sample. We are able to observe the 5 most intense Raman active modes at 131, 305, 365, 496 and 630 cm$^{-1}$ for all the samples. The spectrum is more clear for the In$_2$O$_3$/MgO films and bulk In$_2$O$_3$ powder samples than in the other In$_2$O$_3$ films on sapphire where the sapphire (0001) and (1102) Raman modes interfere with the In$_2$O$_3$ Raman modes, as shown in Fig 4.4. The intense Raman peaks observed in all thin film samples suggest that these films are highly crystalline, consistent with our XRD and microscopic observations.

### 4.2.3 PERSISTENT PHOTOCONDUCTIVITY (PPC) IN In$_2$O$_3$ THIN FILMS

Persistent photoconductivity (PPC) is a light induced change in conductance persisting after irradiation. This has been observed in numerous semiconductors, including wide band gap semiconductors such as ZnO [168] and III-V compound semiconductors [169]. There are various models for explaining the PPC effect in various systems [170].

We have investigated the effect of ultra violet (UV) electromagnetic irradiation on the electrical and optical properties of In$_2$O$_3$ thin films. We used a high power UV light emitting diode (LED) (Nichia, NCSU033A) having a central wavelength of 365 nm, with a full width at half maximum of 6 nm, to irradiate the samples. The resistivity was measured before, during, and after LED illumination using a Keithley 6527A electrometer. The change in the resistance of the In$_2$O$_3$ films upon UV illumination with an intensity of 225 mW/cm$^2$ is shown in Fig 4.5(a).

The resistance changes by approximately two orders of magnitude within the first 3 min of illumination. We observe some sample to sample variation, as shown in Fig 4.5(a), and tentatively attribute this difference to variations in microstructure among the different films. We also investigated the effect of incident power and found that increasing power increases the rate of this drop in resistance but does not affect the saturation value, as shown in Fig
Figure 4.5: (a) Sharp resistance changes observed upon illumination of an In$_2$O$_3$ thin films with a high intensity (∼ 225mW/cm$^2$) UV LED at 365 nm, with some sample to sample variation lying within the limits indicated by the two curves from samples A and B. Inset shows the results of an In$_2$O$_3$ film to the red, green and UV LEDs, with nearly same intensity. (b) Change in resistance of In$_2$O$_3$ thin film with different UV LED incident power, as indicated with applied voltage at the corresponding time in the plot.

4.5(b). This excludes any possibility of sample heating during UV irradiation. To probe the wavelength dependence of this effect, we conducted experiments with red (626 nm) and green (569 nm) LEDs at 1.6 mW and 1 mW respectively. These do not produce any discernible change in resistance, as shown in inset of Fig 4.5(a), whereas when sample was illuminated with UV LED with a reduced intensity of ∼1 mW/cm$^2$, we observe a significant drop in resistance. We also conducted room temperature Hall effect measurements at H=±4 T with a variable current from 5-100 µA on as prepared samples, before to and after the UV illumination. We observed that before illumination the as prepared In$_2$O$_3$ thin films exhibit n-type conduction with carrier density approximately n=2 × 10$^{18}$ cm$^{-3}$ and have a resistivity of ∼ 2.5Ωcm. After UV illumination for 4 minutes (nearly the same time used for relaxation measurements), we observed an order of magnitude increase in carrier density to n=2 × 10$^{19}$ cm$^{-3}$, suggesting that the observed change in resistance can be predominantly attributed to an increase in the number of carriers in the system.

Motivated to the this change in resistance and desiring to understand the modification of In$_2$O$_3$ electronic structure after UV illumination, we conducted the NIR-UV-Vis reflectance
Figure 4.6: (a) Optical absorption \((\alpha \ast E)^2\) versus E for the In\(_2\)O\(_3\) thin film before (red circles) and after (blue circles) UV irradiation. The dashed lines indicate the optical absorption edges. (b) Time decay of the conductance of In\(_2\)O\(_3\) thin film at different temperatures: 200 K, 275 K, 300 K, 325 K and in air (at 300 K). The dashed lines show fits to stretched exponentials. The solid line shows a fit to the logarithmic relaxation.

and transmittance measurements on both the as prepared and UV-illuminated samples, using a Perkin-Elmer Lambda 900 spectrometer. The incident power of the spectrometer source was kept very low, <10 \(\mu\)W, to minimize any possible perturbation of the electronic structure during measurements. The measured reflectance and transmittance data were used to estimated the absorption coefficient \(\alpha\). The \((\alpha \ast E)^2\) versus energy plots for both as prepared and UV illuminated samples are shown in Fig 4.6. We observed that the optical band edge increased from 3.2 eV to 3.31 eV after UV illumination.

The relative increase in the optical band edge upon UV illumination can be attributed to the filling of the conduction band with additional n-type carriers, producing by a Burstein-Moss shift [123, 122]. The Burstein-Moss shift \(\Delta E_{BM}\) using the free electron approximation is given by

\[
\Delta E_{BM} = \frac{\hbar^2}{8\pi^2m^*}(3\pi^2n_e)^{2/3}
\]  

(4.2)

where \(m^*\) is the electron effective mass, \(\hbar\) is the Planck constant and \(n_e\) is electron
carrier concentration. Thus using the observed energy shift $\Delta E \sim 0.11$ eV and the effective mass $m^*$ of the electron $\sim 0.3$, the calculated the carrier concentration is $n=2.4 \times 10^{19} \text{cm}^{-3}$. This increase in carrier concentration is consistent with our Hall effect measurements on the UV-illuminated films.

The most striking feature of the UV induced conductivity in In$_2$O$_3$ is the long range recombination time for these carriers under ambient conditions (exposed to air at room temperature). The recombination time is on the order of several hours, as shown in Fig 4.6(b). We also illuminated In$_2$O$_3$ thin films at 300 K in a Quantum Design Physical Property Measurement System (PPMS) with negligible oxygen partial pressure and then measured time dependence of the conductance at various temperature. The observed conductance relaxation can be reasonably well described by stretched exponential function $\Delta \sigma/\sigma = \exp[-(t/\tau)^\beta]$, with $\beta$ varying from 0.61 at 275 K to 0.51 at 300 K and to 0.43 at 325 K. The time constant $\tau$, being approximately 10 hours at room temperature, follows Arrhenius behaviour with the activation energy of about 0.3 eV. The relaxation rate decreases with decreasing temperature and is completely suppressed by 200 K. Interestingly, the relaxation of the conductance at 300 K in air, as opposed to vacuum, can be better described by a logarithmic decay, $\Delta \sigma/\sigma = A - B \ln(t/\tau)$, rather than by a stretched exponential. These experimental findings suggest that robust photoconductivity can be initiated in In$_2$O$_3$ thin films by UV irradiation and may persists for many hours under ambient conditions. The stretched exponential relaxation in oxygen free environment and logarithmic relaxation in air may be associated with electronic glassy behaviour.

4.2.4 TRANSPORT AND OPTICAL PROPERTIES OF VACUUM ANNEALED In$_2$O$_3$ THIN FILMS

We observed a strong photoconductivity in as grown (AG) In$_2$O$_3$ thin films. In order to further probe and understand the change in electronic and optical properties of oxygen
deficient In$_2$O$_3$ thin films in contrast to the AG In$_2$O$_3$ thin films, we conducted detailed structural, microstructural, optical and electronic studies for both as prepared and vacuum annealed samples. The structural and microstructural properties of the as prepared In$_2$O$_3$ films are practically identical to that described in the previous sections. The XRD pattern for both the as prepared and vacuum annealed In$_2$O$_3$ films is shown in Fig 4.2, indicating highly textured thin films along (222) axis. After vacuum annealing, the Bragg peaks become sharper than those measured for the as prepared sample. This indicates that vacuum annealing at higher temperature improves the crystalline quality.

The UV-Vis-NIR from 175 to 3300 nm was used to measure the optical reflectance and transmittance, as shown in Fig 4.7(a). Both the as prepared and vacuum annealed thin films are transparent throughout the visible region of electromagnetic spectrum, having transmittance approximately 85%.

The absorption coefficient was calculated using these reflectance and transmittance data and the $(\alpha \ast E)^2$ versus energy E are plotted in Fig 4.7(b). The optical absorption edge was determined by extrapolating the linear region for $\alpha \ast E)^2 < 10^{10}$ to E=0. The optical band edges for the as deposited and vacuum annealed samples are $\sim$3.2 and 3.6 eV respectively. This large optical band gap explains the transparency of these films over entire visible spectrum, as seen in the transmittance plots in Fig 4.7(a). We assume that this increase in the optical band edge is mainly due an increase in the carrier concentration filling the conduction bands, causing the Burstein-Moss shift. Using the observed Burstein-Moss shift $\Delta E_{BM} = 0.4 eV$ and electron effective mass $m^* = 0.3 m_e$ for In$_2$O$_3$ [171], the estimated carrier concentration is $\sim 2.49 \times 10^{20} \text{ cm}^{-3}$. This value is in good agreement with the carrier density calculated using the plasmon frequency and room temperature Hall measurements on vacuum annealed samples.

We applied the Drude model to analyze the optical response of these highly degenerate vacuum annealed In$_2$O$_3$ thin films and fit the reflectance data using the plasmon frequency
Figure 4.7: (a) UV-Vis-NIR transmission and reflection spectra for as grown and vacuum annealed In$_2$O$_3$/Sap thin films. (b) Optical absorption $(\alpha \cdot E)^2$ versus energy $E$ for as grown and vacuum annealed In$_2$O$_3$/Sap thin films
\( \omega_p \) and damping constant as fitting variables. We determined that the plasmon peak is \( \sim 0.48 \) eV. Using this value for \( \omega_p \) and high frequency dielectric constant \( (\epsilon_\infty = 3.964) \) [172, 173] and electron effective mass \( (0.3m_e) \) [171], appropriate for In\(_2\)O\(_3\), we calculated a carrier density of \( \sim 2.1 \times 10^{20} cm^{-3} \) for the vacuum annealed In\(_2\)O\(_3\) films. This is consistent with the value estimated from the Burstein-Moss shift and room temperature Hall effect measurements.

The calculated mobilities, extracted from Hall effect measurements, for these as prepared and vacuum annealed thin films are \( \sim 1cm^2V^{-1}s^{-1} \) and \( \sim 40cm^2V^{-1}s^{-1} \) respectively. This is somewhat surprising since the as deposited In\(_2\)O\(_3\) thin film have a larger concentration of scattering defects than the vacuum annealed film, despite the additional oxygen vacancy defects present in the latter sample. These microstructural differences can also be seen in the XRD patterns, where the diffraction peaks become narrower after vacuum annealing, indicating a reduction in structural defects, even with increased carrier concentrations.

We conducted temperature dependent resistivity measurements for both as deposited and vacuum annealed In\(_2\)O\(_3\) films samples from 10 K to 350 K, are shown in Fig 4.8.

As deposited In\(_2\)O\(_3\) films show semiconducting behaviour, while vacuum annealed samples
exhibit metallic resistivity. The resistivity of the vacuum annealed film is almost constant over the entire temperature range, which implies that the carrier concentration and mobility remain almost constant. The increase in carrier concentration by two orders of magnitude and corresponding increase in Hall mobility produce a large drop in resistivity in the vacuum annealed In$_2$O$_3$ films. The mobility of these vacuum annealed thin films are comparable to the values found in TCOs used in many devices, suggesting that oxygen deficient In$_2$O$_3$ may also be suitable for these applications. The figure of merit for typically used to evaluate conducting oxides is $F_H = T^{10}$, where $T$ is optical transmittance at a specific wavelength ($\lambda = 550\, \text{nm}$) and $R_s$ is the sheet resistance in unit of $\Omega/\square$. The $F_H$ for vacuum annealed In$_2$O$_3$ thins film is $\sim 1.2 \times 10^{-2} \Omega/\square$. This value is somewhat lower, but still comparable to that of commercial ITO thin films $\sim 5.9 \times 10^{-2} \Omega/\square$.

As oxygen deficient films often oxidize rapidly in ambient conditions, we also tested the stability of the electrical properties of these samples. The vacuum annealed In$_2$O$_3$ thin films were stored under ambient conditions for an extended time after the initial measurements. Hall measurements repeated six months after our initial studies obtained identical (within the experimental uncertainty) values for the carrier concentration, mobility, and resistivity. This stable increase in the optical transmittance together with increased electrical conductivity and mobility make vacuum annealed In$_2$O$_3$ films potentially useful as a transparent conducting oxide without requiring chemical doping.

### 4.2.5 CATION AND ANION VACANCY DEFECTS AND THE ONSET OF FERROMAGNETISM IN VA In$_2$O$_3$ THIN FILMS

We found that heat treatment under high vacuum significantly modifies the electronic structure and electrical conductivity of In$_2$O$_3$ films. These vacuum annealed films become highly conducting and remains transparent over the entire visible region of the electromag-
netic spectrum. Recent studies by Panguluri et al. [28] have shown that vacuum annealed films can also exhibit room temperature ferromagnetism and \( \sim 55\% \) spin polarization. They proposed that both oxygen anion and indium cation vacancies may play an important role for the onset of ferromagnetism in these systems.

Motivated by these observations we have investigated the magnetic properties of as-prepared and vacuum annealed \( \text{In}_2\text{O}_3 \) films using a Quantum Design MPMS and the microstructural properties using Rutherford Back Scattering (RBS) and high resolution transmission electron microscope (HRTEM). The room temperature magnetization curves for both samples are shown in Fig 4.9. These data are corrected by subtracting the diamagnetic background arising from the sapphire substrate. The inset in Fig 4.9, shows the magnetization data without any background correction. The magnetization of the as prepared \( \text{In}_2\text{O}_3/\text{Sap} \) thin films is negligible; we observe a significant increase in magnetization reaching to \( \sim 0.5\text{emu/cm}^3 \) after vacuum annealing at 600 °C for 9 hours.

In order to investigate the oxygen vacancies created in these samples during the vacuum annealing process, we conducted Rutherford Back Scattering (RBS) measurements using 2.704 MeV He\(^+\) ions. The results are plotted in Fig 4.10. In these backscattering experiments the \( \alpha \) beam was collimated to 1 mm and was at normal incident to the films. The backscattered particles were detected by a silicon surface barrier detector subtending a solid angle of 1.2 msr, set at a laboratory angle of 170°. The experimental backscattered spectra were simulated using Ziegler-Biersack stopping cross-sections by SIMNRA [175] software, to obtain the atomic composition and thickness of the films. The areal densities of In and O in as prepared films are \( \sim 23.97 \times 10^{17} \text{ atoms/cm}^2 \) and \( \sim 38.76 \times 10^{17} \text{ atoms/cm}^2 \) respectively. This suggests that the as prepared \( \text{In}_2\text{O}_3 \) thin films are highly stoichiometric having a \( \text{In}:\text{O} \) ratio of \( \sim 38.2:61.8 \), equal to 2:3 within the instrumental (approximately 5% atomic concentration) error limits. The areal densities of In and O for the vacuum annealed \( \text{In}_2\text{O}_3 \) thin films decrease to \( 23.47 \times 10^{17} \text{ atoms/cm}^2 \) and \( 30.92 \times 10^{17} \text{ atoms/cm}^2 \) respectively,
Figure 4.9: M(H) curves for as grown (closed blue circles) and vacuum annealed (open red circles) $\text{In}_2\text{O}_3$/Sap thin films (corrected for diamagnetic contributions). The bottom right inset shows the unprocessed data. The top left inset shows the magnetization curves of bare vacuum annealed sapphire.
Figure 4.10: Rutherford backscattering plots for (a) as grown (b) vacuum annealed In$_2$O$_3$/Sap thin films. The red lines show theoretical simulations indicating a In:O atomic ratio $\sim$ 43:57. This suggests that vacuum annealed In$_2$O$_3$ films are highly oxygen deficient, with a non-stoichiometry of approximately $\sim$ 7%.

We believe that removing the oxygen leaves an In rich surface after vacuum annealing. Due to the high annealing temperature, In evaporates from the surface, resulting in small reduction in the thickness of In$_2$O$_3$ films. These measurements suggests that the increase in conductivity on vacuum annealing may be due to, at least in part, to additional charge carriers coming from the oxygen vacancies. To probe the influence of defects on the microstructure of these samples, we conducted high resolution transmission electron microscopy (HRTEM) for both as prepared and vacuum annealed In$_2$O$_3$ thin films. We imaged In$_2$O$_3$ crystallites,
Figure 4.11: High-resolution TEM micrographs of 100 surface regions for (a) as grown (AG) and (b) vacuum annealed (VA) In$_2$O$_3$ samples. (c) A magnified view of a section of (b) with arrows showing distortions in the crystal lattice. The square region of the HRTEM image in (c) corresponds to a unit cell of In$_2$O$_3$ shown in the ball and stick model projected along (100) plane. The inset ((i) and (ii)) in (c) are the simulated HRTEM images with (i) a oxygen vacancy and (ii) a oxygen vacancy with two adjacent In atoms clustering model. (d) HRTEM image of high VA In$_2$O$_3$ just below amorphous surface region. The top of surface is highly defective compared to the bulk (\textasciitilde 10 nm below surface). The short arrows indicate the dark region, showing typical In clustered regions. The long arrow shows an edge dislocation.

obtained by scratching thin films onto the carbon coated formvar Cu grids, to avoid any accidental modifications during the ion beam milling process typically for thinning samples for imaging. HRTEM phase contrast images were acquired using a JEOL-2010 Fas TEM microscope operated at 200 kV with a point resolution of 0.23 nm and lattice resolution of 0.14 nm.

Fig 4.11(a) and (b) shows representative HRTEM images with the beam oriented along the $\bar{1}100\bar{6}$ directions of the In$_2$O$_3$ lattice. The samples have 50 nm wide and \textasciitilde 1\(\mu\)m long columnar grains and the images are taken from the top surface of these grains. As deposited In$_2$O$_3$ particles show a perfectly ordered crystalline lattice to the very edge of the particle,
whereas vacuum annealed In$_2$O$_3$ particles have $\sim$2-3 nm thick amorphous layers at the surface. In addition to this surface disordered layer, we observe a number of defects in the interior of the particles several nanometers below the top surface, as shown in Fig 4.11(b). Such defects are not seen in the as deposited In$_2$O$_3$ nanoparticles, Fig 4.11(a). The observation of this amorphous layer is consistent with the considerable surface reconstruction inferred from the RBS studies.

A magnified region of the HRTEM image from Fig 4.11(b) is shown in Fig 4.11(c) with arrows indicating the lattice distortions, which reflect the presence of defects in the In$_2$O$_3$ unit cells. The In$_2$O$_3$ structure, presented as a ball and stick model projected along the $<010>$ direction, is shown in Fig 4.11(c). As mentioned in earlier discussion, In$_2$O$_3$ exhibits the cubic bixbyte structure (space group Ia3), with one quarter of the In atoms located in trigonally compressed octahedral (b sites) and other three quarter of the In atoms located in highly distorted octahedral (d sites), Fig 4.1(b). We simulated the HRTEM images by introducing O vacancies and In-In clustering with O vacancies. The HRTEM simulations projected along the $<010>$ directions with a missing oxygen atom and for an oxygen vacancy with an adjacent In pair are shown in Fig 4.11(c) insets (i) and (ii) respectively. The representative simulations of different defect models provide an indication of the types of defects that could produce the HRTEM images seen in the vacuum annealed In$_2$O$_3$ samples. The arrows in Fig 4.11(d) indicate defects observed in the HRTEM image for the vacuum annealed sample that are similar to the simulated HRTEM images shown in Fig 4.11(c) and 4.11(d). These results strongly suggest that there are both oxygen vacancies and In vacancies (arising from In-In clustering) in the vacuum annealed samples, although the real defect structures may be even more complicated that what we have used for these simulations.

The top and bottom edges of Fig 4.11(d) belong to the region near the amorphous surface and to the interior of the vacuum annealed In$_2$O$_3$ crystallite at a distance of 10 nm from the surface. We find that the defect density is higher near the surface than in the
interior of the crystallites, with a typical defective regions shown by arrows in Fig 4.11(d). There are occasional edge dislocations, which are seen in both the as prepared and vacuum annealed In$_2$O$_3$/Sap films, indicated by a long horizontal arrow in Fig 4.11(d). The defect concentration close to these dislocations is higher in vacuum annealed In$_2$O$_3$ samples. The defect density estimated from the HRTEM images are on the order of $\sim 10^{13}$ cm$^{-2}$ to $10^{14}$ cm$^{-2}$, with approximate bulk densities $\sim 3 \times 10^{19}$ cm$^{-2}$ to $10^{21}$ cm$^{-3}$, corroborating the RBS observations that vacuum annealed In$_2$O$_3$ thin films exhibit significant non stoichiometry at the surface and continues to the few tenths of a nanometer below the surface.

These vacuum annealed In$_2$O$_3$ thin films exhibit a high concentration of intrinsic donor defects, especially oxygen vacancies, resulting in a two orders of magnitude increase in the carrier density $\sim 10^{20}$ cm$^{-3}$, concomitant with room temperature ferromagnetism [28]. It has been proposed that cation vacancies would also be necessary for the development of ferromagnetism in these non stoichiometric oxides [28]. Recent theoretical studies also suggest that oxygen depleted In$_2$O$_3$ surfaces with In vacancies should become ferromagnetic [176]. Our experimental results suggest that both oxygen anion and In cation vacancies coexist in vacuum annealed In$_2$O$_3$ thin films, where the presence of cation vacancy defects is inferred from evidence for In-In clustering. These defect densities are estimated to be approximately $\sim 10^{14}$ cm$^{-2}$, which is consistent with the measured carrier concentration $\sim 10^{20}$ cm$^{-3}$. Thus these vacuum annealed In$_2$O$_3$ thin films having oxygen vacancies as self-doped donors and indium clusters as self compensated magnetic acceptors could exhibit room temperature carrier-mediated ferromagnetism [28] and substantiating the the theoretical predictions [176, 28].
4.2.6 STRONG PLASMON OBSERVATION AND THEIR SWITCHABILITY IN In$_2$O$_3$ THIN FILMS

We have observed that In$_2$O$_3$ shows a number of striking materials properties including a persistent photocurrent, transparent conductivity over the visible spectrum, ferromagnetism, and ferromagnetism above room temperature. In this section we will explore the plasmon excitations in the infrared region of electromagnetic spectrum introduced after vacuum annealing, along with their suppressing and re-appearance on heat treatment in air and in vacuum respectively.

The In$_2$O$_3$ thin films used for this work were prepared using rf magnetron sputtering process described above. The as prepared In$_2$O$_3$ thin films were vacuum annealed at 600 °C for 9 hours. The X-ray diffraction patterns and scanning electron micrographs are functionally identical to those shown in Fig 4.2. We have investigated the onset of plasmon in vacuum annealed In$_2$O$_3$ thin films using UV-Vis-NIR spectroscopy and correlate these measurements to the n-type defect energy levels providing excess carriers into the vacuum annealed In$_2$O$_3$ system using room temperature photoluminescence (PL) spectrum.

We measured the reflectance and transmittance to calculate the absorbance $\alpha$ and plot the reflectance and $(\alpha \ast E)^2$ versus energy $E$ in Fig 4.12(a). This is done for as grown (AG) samples, vacuum annealed (at 600 °C for 9 hours) (VA) samples, and samples reannealed in air (at 600°C for 9 hours) (AA). The reflectance curve for the vacuum annealed In$_2$O$_3$/Sap thin film exhibits a large reflection edge due to the plasmon excitation in the lower energy region of the spectrum, as seen in Fig 4.12(b). At higher energies, we observe well defined fringes due to optical interference between waves reflecting from the substrate interface and the surface. The estimated thickness from these interference fringes is in good agreement with the cross-sectional SEM micrographs, shown in Fig 4.3. The optical absorption edges for these AG, VA and AA In$_2$O$_3$ thin films were determined by extrapolating the linear region of the $(\alpha \ast E)^2$ curves to the energy $E=0$. The optical absorption edges for the AG,
Figure 4.12: (a) Optical absorption $(\alpha \times E)^2$ versus energy for as grown (AG), vacuum annealed (VA) and re air annealed (RAA) In$_2$O$_3$/Sap thin films. (b) Optical absorption spectrum plotted on a reduced scale to show the plasmon peak near 0.5 eV in VA In$_2$O$_3$/Sap.
VA and AA samples are of the order of 3.3±0.1 eV, 3.6±0.1 and 3.3±0.1 eV respectively. In the low energy spectrum we observe the onset of plasmon absorption at ∼0.5 eV for vacuum annealed In$_2$O$_3$ thin film, as shown in the $(\alpha * E)^2$ versus energy E plots, Fig 4.12(b). This onset of plasmon absorption ∼0.5 eV in vacuum annealed In$_2$O$_3$ thin films is attributed to the generation of excess electron charge carriers due to oxygen vacancies created during vacuum annealing. The Drude model was applied to analyze the optical response of vacuum annealed In$_2$O$_3$/Sap films and to simulate the reflection data using plasmon frequency and damping constant as fitting variables. We observed the plasmon frequency at ∼0.5 eV, consistent with the plasmon absorption peak observed in absorption spectrum, Fig 4.12(b). The estimated carrier concentration, using a plasmon frequency of $\omega_p$=0.5 eV, a high frequency dielectric constant of $\epsilon_{\infty} = 3.964$ [172, 173], and an electron effective mass of $0.3m_e$ [171] is $\sim 2.1 \times 10^{21}$ cm$^{-3}$. This estimated carrier concentration estimated from the plasmon is in good agreement with our room temperature Hall measurement.

When the vacuum annealed In$_2$O$_3$/Sap film was reannealed in air at 600 °C for 9 hours, we found that the plasmon reflection edge and corresponding plasmon absorption peak disappears, or is shifted to an energy range below the resolution of the spectrometer, similar to the as grown sample. We suggest that the reannealed In$_2$O$_3$ film become more stoichiometric, compositionally similar to the as prepared In$_2$O$_3$ thin film, reducing the number of oxygen vacancies, resulting in a reduction of the carrier concentration. This was confirmed by our room temperature Hall measurements where the carrier concentrations for the as prepared and air annealed In$_2$O$_3$ thin films were found to be very similar, $n \sim 10^{18}$ cm$^{-3}$.

We carried out photoluminescence (PL) measurements using a 514.5 nm green laser as our excitation source for the as grown and vacuum annealed In$_2$O$_3$ films and the bare sapphire substrate, as shown in Fig 4.13. The PL spectrum for the air-annealed In$_2$O$_3$ thin films is practically identical to the as grown and is not plotted. The first order Raman spectrum for In$_2$O$_3$ films was observed near an excitation energy of 2.41 eV, as shown in Fig 4.13. We also
Figure 4.13: Room temperature photoluminescence (PL) spectrum for as grown (AG), vacuum annealed (VA) In$_2$O$_3$/Sap thin films and a bare sapphire substrate, collected using a 514.5 nm wavelength excitation source. The spectrum near 2.4 eV show the 1st order Raman spectrum of respective samples. The insets showing schematic energy diagram for AG and VA In$_2$O$_3$ thin films with oxygen vacancy states $\sim$1.9 eV for the VA In$_2$O$_3$ thin film.

We observe a very broad yet clearly discernible feature centered at $\sim$1.9 eV, which is not seen in either the as grown nor air annealed In$_2$O$_3$ thin films, Fig 4.13. We propose that this peak at $\sim$1.9 eV in the photoluminescence spectrum, seen only in the vacuum annealed sample, is associated with the oxygen vacancy defect energy level with respect to the valance band edge $E_v$, schematically shown as an inset in Fig 4.13.

We have observed the onset of a plasmon excitation in vacuum annealed In$_2$O$_3$, which is mainly associated to the collective excitation of excess electrons donated by oxygen vacancies. These oxygen vacancies form electronic defect states at $\sim$1.9 eV, as determined by photoluminescence measurements. These defect states can be filled with oxygen by reannealing the defect-rich sample in air at 600 °C for 9 hours. This heat treatment in air leads to a decrease in carrier concentration by removing the oxygen vacancy defects and thus also suppressed the plasmon found in the vacuum annealed films. The plasmon observed in vacuum annealed In$_2$O$_3$ thin film systems is qualitatively different to that observed in oxygen rich InN, discussed in chapter 3, since the InN plasmon can not readily be switched on and
off by annealing in different atmospheres. This makes In$_2$O$_3$ more promising for certain IR applications.

4.3 CONCLUSION

We have investigated the optical, electronic, and magnetic properties of as grown stoichiometric and vacuum annealed oxygen deficient In$_2$O$_3$ thin films and correlated these properties compositional and microstructural changes produced by annealing. The as grown In$_2$O$_3$ films show strong persistent photoconductivity (PPC) with a very long recombination time, even under ambient conditions. Oxygen deficient In$_2$O$_3$ thin films show high optical transparency $\geq 85\%$ with enhanced electrical conductivity, which is stable over a very long time. These highly degenerate oxygen deficient thin films also show strong plasmon absorption at a relatively low energy ($\sim 0.5$ eV). More interestingly this plasmon absorption can be turned off by reannealing the In$_2$O$_3$ films in air. Additionally these oxygen deficient In$_2$O$_3$ thin films show ferromagnetism above room temperature. Our detailed microstructural and high resolution transmission electron microscopy (HRTEM) studies suggest that vacuum annealing not only introduces oxygen vacancies but also indium vacancies due to promoting In-In clustering. The simultaneous presence of oxygen and indium vacancies in In$_2$O$_3$ may provide the mechanism for the development of carrier mediated ferromagnetism in this material. Taken together, these studies suggest that undoped, but defect-rich, In$_2$O$_3$ could be incorporated into a wide range of future opto-electronic and spintronic devices.
Chapter 5

YMn$_{1-x}$In$_x$O$_3$ MULTIFERROIC -MAGNETIC, THERMAL AND MAGNETODIELECTRIC PROPERTIES

5.1 INTRODUCTION

YMnO$_3$ is a widely studied type-I multiferroic system, where ferroelectric ordering develops at the Curie temperature $T_C \sim 900K$ and an A-type antiferromagnetic ordering arises below the Neel temperature $T_N \sim 75K$ having non-collinear Mn spins oriented in a triangular arrangement [177, 178]. YMnO$_3$ thus exhibits multiferroic properties at temperatures below this magnetic phase transition. The system crystallizes into a hexagonal crystal structure with the centrosymmetric space group $P6_3/mmc$ in the paraelectric phase, which changes to the $P6_3cm$ space group in ferroelectric phase. The hexagonal crystal structures of YMnO$_3$ in the paraelectric and ferroelectric phases are shown in Fig 5.1. Recently, the onset of
ferroelectricity has been attributed to a size mismatch between Y and Mn, which induces a trimerization-type structural phase transition causing the buckling of the layered MnO$_5$ polyhedra, accompanied by displacement of the Y ions, leading to a net polarization [69, 179]. Previous studies had argued that the ferroelectricity is due to an off-center distortion of the Mn ion towards one of the apical oxygen ions [180].

Hexagonal YMnO$_3$ has been extensively studied as a material for non-volatile ferroelectric memory [181] and, more recently, its multiferroic properties have been explored showing coupling between ferroelectric and magnetic order parameter [63, 182]. In order to more fully understand the magnetoelectric coupling in this material, we investigated the effects of incorporating non-magnetic In dopants at Mn magnetic cation sites. In this section, we will discuss the magnetodielectric properties of YMn$_{1-x}$In$_x$O$_3$ system at the antiferromagnetic

Figure 5.1: YMnO$_3$ crystal structure with trigonal bipyramids representing MnO$_5$ polyhedra and gray spheres represent Y ions. (a) a stack of two consecutive MnO$_5$ layers and the sandwiched Y layer, looking down the c axis in the paraelectric phase and (b) A view of the ferroelectric phase from perpendicular to the c-axis, showing the layered nature of YMnO$_3$ [69].
5.2 EXPERIMENTS AND RESULTS

5.2.1 SYNTHESIS OF BULK YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES

YMn$_{1-x}$In$_x$O$_3$ ceramic samples having compositions ranging from $x = 0$ to $x = 1$ were prepared by solid state synthesis. Stoichiometric ratios of Y$_2$O$_3$, Mn$_2$O$_3$ and In$_2$O$_3$ powders were mixed thoroughly in ethanol to ensure the homogeneity. Uniformly mixed samples were pressed into pellets under high pressure. The pressed pellets were calcinated at elevated temperatures followed by intermediate grinding. The detailed of sample preparation is discussed in somewhere else [183].

5.2.2 STRUCTURAL CHARACTERIZATION OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES

The structural investigation of YMn$_{1-x}$In$_x$O$_3$ these ceramic samples was carried out using X-ray powder diffraction (XRD). The $\theta - 2\theta$ powder XRD patterns were collected with RIGAKU MINIFLEX II diffractometer using CuK$_\alpha$ radiation and a graphite monochromator. The XRD patterns for YMn$_{1-x}$In$_x$O$_3$ ($0 \leq x \leq 1$) are shown in Fig 5.2(a). The entire XRD spectrum can be fully indexed to the hexagonal P63cm structure without any evidence for a secondary phase. A relative shift in the diffraction peak positions was observed as the In fraction in YMn$_{1-x}$In$_x$O$_3$ was increased monotonically from 0 to 1. These peaks show the expected behaviour and follow Vegard’s law as $a(YMn_{1-x}In_xO_3) = a(YMnO_3) \times (1-x) + a(YInO_3) \times x$; where $a$ is the lattice constant. The variation of lattice parameter $a$, $c$ and
Figure 5.2: (a) XRD pattern for YMn$_{1-x}$In$_x$O$_3$ samples, as indicated by legend on the right of the figure. (b) and (c) Vegard’s law plots for YMn$_{1-x}$In$_x$O$_3$ showing the systematic change in lattice parameter with In content.

The ratio $c/a$ with respect to the indium content ($x$) is shown in Fig 5.2(b) and (c) and is in good agreement with the Vegard’s law. The linear variation in $a$ and $c$ lattice parameter are consistent with the length of the apical M-O bond increasing as the In fraction increases in YMn$_{1-x}$In$_x$O$_3$.

5.2.3 MAGNETIC AND THERMAL PROPERTIES OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES

The magnetic properties of YMn$_{1-x}$In$_x$O$_3$ samples were measured using a Quantum Design MPMS SQUID magnetometer and a Quantum Design Physical Properties Measurement System (PPMS). The temperature dependent magnetic susceptibilities for the YMn$_{1-x}$In$_x$O$_3$ samples for $x = 0$, 0.25, 0.5 and 0.75 are plotted in Fig 5.3(a).

We observe a systematic decrease in the high temperature susceptibility with increasing
Figure 5.3: (a) Temperature dependent magnetic susceptibility at $\mu_0H = 0.5T$ for YMn$_{1-x}$In$_x$O$_3$ samples with the inset showing the background corrected susceptibility for $x=0$ and $x=0.25$ samples. (b) C/T versus T, for YMn$_{1-x}$In$_x$O$_3$ samples.

$x$, consistent with replacing Mn$^{3+}$ ions with the non magnetic In$^{3+}$ ions. The Curie-Weiss temperature $\Theta_{CW}$, estimated from the high temperature susceptibility data varies systematically from -337 K for $x = 0$ to -325 K, -240 K and -83 K for $x = 0.25$, 0.5 and 0.75 respectively. This decreasing Curie-Weiss temperature suggests that the strong AFM interactions are continuously reduced with an increase in the In fraction. The effective moment per Mn estimated from the high temperature susceptibility is $4.2\pm0.5\,\mu_B$ for all samples. At low temperatures, the paramagnetic Curie-Weiss behaviour for the $x = 0.5$ and 0.75 samples lead to a larger susceptibility than in the magnetically ordered $x = 0$ and 0.25 samples. The magnetic anomalies associated with the development of antiferromagnetic order for the $x=0$ and $x=0.25$ samples are shown in the inset of Fig 5.3(a), where magnetic data was corrected for the background paramagnetic contribution. The observed magnetic transition $T_N = 72$ K for YMnO$_3$ is in agreement to the earlier studies and is suppressed to $T_N = 42$ K for the
YMn_{0.75}In_{0.25}O_3 sample. The magnitude of this suppression is very similar to what has been reported for Ga substituted YMnO_3, having a similar fraction of non-magnetic Ga ions replacing Mn^{3+} ions. We do not observe any clear magnetic anomalies for YMn_{1-x}In_xO_3 samples having x ≥ 0.5, indicating that the antiferromagnetic transition temperature is pushed below T = 20 K, where the paramagnetic Curie tail obscures the magnetization data.

We also conducted specific heat measured on these YMn_{1-x}In_xO_3 samples using the standard option on the Quantum Design PPMS. We used approximately 50 mg of each sample and mixed thoroughly with the same mass of a fine Ag powder. The homogeneously mixed powder was pressed into small pellets to ensure good thermal contact throughout the entire sample. The silver background contribution was measured separately and subtracted from the (YMn_{1-x}In_xO_3 + Ag) heat capacity data. The Ag background corrected temperature dependent specific data, measured at zero applied field, for different YMn_{1-x}In_xO_3 samples is shown in Fig 5.3(b). The YMn_{1-x}In_xO_3 samples with smaller In fractions exhibit a clear peak in heat capacity at the antiferromagnetic phase transition, while the In rich samples do not show any clear anomalies. For x=0.5 and above, the heat capacity is roughly the same for all compositions, confirming that the differences in specific heat arise solely from the magnetic ordering of Mn ions and not from any significant difference in lattice contributions. Estimating the lattice contribution to the YMnO_3 heat capacity from the YMn_{0.5}In_{0.5}O_3 data, and neglecting the slight difference in mass between Mn and In ions, we observed that the magnetic entropy between 25 K and 85 K associated with Mn spin ordering is approximately 5.3 J/mole K. This considerably smaller than the Rln5=13.4 J/mole K expected for the full ordering of S=2Mn^{3+} ions. We attribute this discrepancy to the considerable entropy developing above T = 85 K, which is excluded from our estimate, as well as with errors associated with correcting for the silver background contributions.
5.2.4 DIELECTRIC AND MAGNETODIELECTRIC PROPERTIES OF YMn$_{1-x}$In$_x$O$_3$ CERAMIC SAMPLES

The temperature dependent dielectric properties and isothermal magnetocapacitance for different YMn$_{1-x}$In$_x$O$_3$ samples were investigated using an Agilent 4284A Precision LCR meter and with temperature and magnetic field control provided by the PPMS. The samples were pressed pellet having a parallel plate geometry with electrodes fashioned from silver epoxy. The relative temperature dependent dielectric constants for the x = 0.1, 0.25, 0.5 and 0.75 YMn$_{1-x}$In$_x$O$_3$ samples, scaled to the value at T = 80K, just above the transition temperature for YMnO$_3$ are shown in Fig 5.4(a). The very small change in dielectric constant coincident with the antiferromagnetic ordering are indicated by the arrows.

The antiferromagnetic ordering temperature $T_N$ is $\sim 60$ K and 42 K for x = 0.1 and 0.25 YMn$_{1-x}$In$_x$O$_3$ samples respectively, as compared to $\sim 72$K for undoped YMnO$_3$ sample. There is no dielectric anomaly for x $\geq 0.5$ with in the temperature range under investigation, consistent with our magnetic and heat capacity measurements. The field dependence of the relative change in the capacitance measured at T=10 K are shown in Fig 5.4(b) for different YMn$_{1-x}$In$_x$O$_3$ samples. This temperature is below the magnetic ordering temperature for the x = 0, 0.1 and 0.25 samples and above any possible ordering temperature for x = 0.75 samples. The x = 0 and 0.1 samples exhibit negligible magnetocapacitive coupling, with some small shift in the capacitance observed for the x = 0.25 sample. The x = 0.5 and 0.75 samples show significant larger field induced shifts in capacitance, with the change in capacitance reaching over 0.05% in an applied field of $\mu_0H=8T$, as shown in Fig 5.4(b). This large magnetocapacitance suggests that the dielectric constant is coupled to the paramagnetic spins in samples having larger In fractions, which do not order magnetically in the investigated temperature range. The most striking feature of the magnetocapacitive shift is the change of sign between different sample, as shown in Fig 5.4(b). The x=0.5 sample shows positive magnetocapacitance, which changes into negative capacitance for x=0.75 sample.
Figure 5.4: (a) Relative change in capacitance versus temperature for YMn$_{1-x}$In$_x$O$_3$ samples, with the dashed arrow indicating the dielectric anomalies associated with AFM ordering transitions. (b) Magnetic field dependence of the capacitive response with solid bars on the $x=0$, 0.5 and 0.75 curves indicating the scatter in the data before smoothing. The dashed line on the $x=0.75$ curve is the best fit. (c) Temperature dependence of the magnetocapacitive coupling constant for the $x=0.5$ and $x=0.75$ YMn$_{1-x}$In$_x$O$_3$ samples. (d) Temperature dependence of the AFM ordering transition on $x$ in YMn$_{1-x}$In$_x$O$_3$, extracted from different measurements.
With in the mean field approximation, the relative magnetocapcitve shift is proportional to
the the square of the applied field $\Delta C/C \simeq \gamma H^2$, arising from the lowest order term coupling
P and H allowed by symmetry in the free energy [65], where $\gamma$ is the coupling parameter.
The fit to this functional form is shown in Fig 5.4(b) by the dashed line for the $x = 0.75$
sample. The temperature dependence of the coupling parameter $\gamma$ is plotted in Fig 5.4(c) for
$x=0.5$ and $x=0.75$ samples. We observe that $\gamma(T)$ decreases systematically with increasing
temperature for $x=0.5$ sample, consistent with the reduction in the magnetic susceptibility,
whereas $\gamma(T)$ is negative at lower temperature and crossing over to a positive value at higher
temperatures, as shown in Fig 5.4(c). The dielectric response and the magnetocapacitive
coupling may be highly anisotropic and hence may be different along and perpendicular to
the c-axis, leading to the different $\gamma_\parallel$ and $\gamma_\perp$. Similar studies on YMn$_{1-y}$Ga$_y$O$_3$
find that the $\gamma_\parallel$ component changes sign as $y$ changes from 0 to 0.3, leading to both positive and
negative magnetocapacitive shifts [88]. In our case magnetocapacitance response, shown in
Fig 5.4(b), is the powder average of the anisotropic response, a change in the sign of $\gamma(T)$
could be produced by a a change of sign in $\gamma_\parallel(T)$. However in our measurements, both the
$x=0.5$ and $x=0.75$ samples are paramagnetic over entire temperature range, so it is not clear
why there would be a change in sign either as a function of In fraction or as a function of
temperature.

The thermal, dielectric and magnetic results are summarized in the YMn$_{1-x}$In$_x$O$_3$ phase
diagram, shown in Fig 5.4(d), where antiferromagnetic ordering temperature estimated from
these different measurements is plotted against the In content of YMn$_{1-x}$In$_x$O$_3$ samples. The
AFM transition temperature estimated from different techniques agree with on another,
confirming a single magnetic transition giving rise to the dielectric anomalies even in the
In substituted samples. The scaling of $T_N$ with $x$ can be explained in terms of simple site
dilution by non-magnetic ions. The initial slope of the suppression of $T_N$ with In substitution,
$p = -(\partial T_N/\partial x)/T_N$ is approximately 1.6. This reduction in $T_N$ on substituting non-magnetic
ions is larger than for a three dimensional system where \( p \approx 1.2 \) \[184\] and is more consistent with that expected for Ising spins in two dimensions, where \( p \) varies from 1.6 to 1.9 \[185\]. This confirms the importance of the in-plane interactions among Mn\(^{3+}\) ions in developing long range AFM order.

### 5.3 CONCLUSION

We have investigated the effects of In doping on YMnO\(_3\) and observed a suppression of the multiferroic phase developing below \( T_N \). The transition temperature \( T_N \) decreases linearly with increasing In fraction in YMn\(_{1-x}\)In\(_x\)O\(_3\) system and AFM ordered state vanish for \( x \geq 0.5 \) samples. This AFM suppression is quantitatively consistent with predictions for a diluted two dimensional spin system. We noticed a significant enhancement in the magnetocapacitive coupling with In substitution and the sign of this coupling varies with \( x \). Our study confirms that the substitution of non magnetic In ions for Mn in YMnO\(_3\) system, suppresses AFM ordering without introducing any structural phase transition for entire \( 0 \leq x \leq 1 \) solid solution range while simultaneously enhancing the magnetocapacitive coupling.
Chapter 6

$\text{Ni}_3\text{V}_2\text{O}_8$ MULTIFERROIC

-ELECTRONIC, DIELECTRIC,

AND MAGNETODIELECTRIC

PROPERTIES

6.1 INTRODUCTION

Nickel vanadate ($\text{Ni}_3\text{V}_2\text{O}_8$) is an insulating magnetic material, identified as a magneto-electric multiferroic, which exhibits simultaneous appearance of magnetic and ferroelectric ordering at one particular low temperature magnetic transition $T_{LTI}=6.4\text{K}$ [70, 186]. The system crystallizes in an orthorhombic crystal structure having the $C_{mca}$ space group. Under ambient conditions the system is anisotropic with lattice parameters $a=5.92\,\text{Å}$, $b=11.37\,\text{Å}$ and $c=8.22\,\text{Å}$ although system undergoes distortions associated with low temperature magnetic phase transitions [187]. The $\text{Ni}_3\text{V}_2\text{O}_8$ orthorhombic crystal structure can be characterized by Kagome-like layers of edge sharing $\text{Ni}^{2+}\text{O}_6$ octahedra together with nonmagnetic $\text{V}^{5+}$
ions separating the Ni$^{2+}$ layers. The crystal structure of Ni$_3$V$_2$O$_8$ is shown in Fig 6.1, with Ni$^{2+}$ ions in the lattice. The magnetic layers consisting of Ni$^{2+}$ ions in Ni$_3$V$_2$O$_8$ are buckled producing a Kagome-staircase geometry [188, 70], where the Kagome staircase planes are perpendicular to the crystallographic b-axis.

The Kagome-staircase lattice of Ni$^{2+}$ ions results into two crystallographically inequivalent Ni$^{2+}$ magnetic sites, denoted as cross-tie (Ni$_c$) and spine (Ni$_s$), shown in Fig 6.1. The nearest-neighbour (NN) and second nearest neighbour (SNN) interactions between Ni$_c$ and Ni$_s$ and associated geometrical magnetic frustration lead to a complex magnetic phase diagram [70] and the system undergoes numerous magnetic phase transitions. The Ni$_3$V$_2$O$_8$ system is paramagnetic at temperatures above 10 K without any long range magnetic or ferroelectric ordering. As the system is cooled at zero ($\mu_0H = 0T$) field, long range magnetic ordering develops at $T_H=9.1$ K with an incommensurate spin structure, as shown in Fig 6.1 (b). This phase is referred to as the high temperature incommensurate phase (HTI). Further cooling results into another magnetic transition at $T_L=6.4$ K with incommensurate spin.
structure called the low temperature incommensurate (LTI) phase, Fig 6.1 (c). In addition to these continuous second order phase transition, $\text{Ni}_3\text{V}_2\text{O}_8$ undergoes a first order magnetic phase transition at $T_C = 4.2$ K, into the canted antiferromagnetic (CAF) phase, in which spins are ordered antiferromagnetically along the a-axis, with a small canting along the c-axis, Fig 6.1 (d). There is an additional zero field second order magnetic phase transition at $T'_C = 2.2$ K.

The most striking feature of this complex phase diagram is the onset of ferroelectricity at the LTI phase $T_L=6.4$ K along the b-axis leading to the coexistence of magnetic and ferroelectric order only in the LTI phase. A Landau mean field theory model was developed to explain the multiferroicity of $\text{Ni}_3\text{V}_2\text{O}_8$ [70, 186, 189]. According to this model the Landau free-energy expansion is given by

$$F = a(T - T_H)\sigma_H^2 + b(T - T_L)\sigma_L^2 + O(\sigma^4) + \frac{1}{2\chi_E}P^2 + V \quad (6.1)$$

Where $a$ and $b$ are constants, $T$ is the temperature, $\sigma_H$ and $\sigma_L$ are the magnetic order parameters in the HTI and LTI phases respectively, $\chi_E$ is the electric susceptibility, $P$ is the electric polarization and $V$ is the lowest order trilinear symmetry-allowed magnetoelectric energy term and is given by:

$$V_{LTI} = \sum_\gamma a_\gamma \sigma_H \sigma_L \sin(\phi_H - \phi_L) P_\gamma \quad (6.2)$$

Group theoretical analysis and the symmetry restrictions for $\text{Ni}_3\text{V}_2\text{O}_8$ system allowed the polarization along the b-axis [186], consistent with the experimental observation [190] and is given by

$$P_b \propto a_\gamma \chi_E \sigma_L \sigma_H \quad (6.3)$$

$\text{Ni}_3\text{V}_2\text{O}_8$ exhibits strong magnetoelectric coupling, suggesting cross-control of magnetic and ferroelectric order parameters is possible. In this section, we will discuss in detail the
electric field control of magnetic phase transition in Ni$_3$V$_2$O$_8$ thin films, measured using dielectric spectroscopy, and will construct E-H-T phase diagram. We will also discuss the dielectric critical behaviour using dielectric spectroscopy and room temperature optical and electronic properties of Ni$_3$V$_2$O$_8$ system in both bulk ceramic, single crystal, and thin film geometries emphasizing the intrinsic highly insulating properties, necessary for good ferroelectric properties.

6.2 EXPERIMENTS AND RESULTS

6.2.1 SYNTHESIS OF Ni$_3$V$_2$O$_8$ BULK CERAMIC, SINGLE CRYSTAL AND THIN FILMS

We have used Ni$_3$V$_2$O$_8$ bulk single crystal, ceramic and thin film samples to investigate the magnetoelectric and multiferroic properties of this system. The single crystal samples of Ni$_3$V$_2$O$_8$ system were grown from a BaO-V$_2$O$_5$ flux as described in detail in reference [188]. The polycrystalline powder samples were prepared using a standard solid state reaction technique. Solid powders of NiO and V$_2$O$_5$ were mixed in stoichiometric Ni:V atomic ratio as 3:2. These solid solutions were mixed homogeneously in methanol and ground to produce a homogeneous mixture. This mixture was heated at 600 °C for 6 hours in air. Intermediate grinding followed by this same thermal annealing in air were repeated several (3-4) times to complete the solid state reaction and ensure a fully reacted and uniform composition. This homogeneous solid solution was finally heated at 1000 °C for 2 hours to get single phase Ni$_3$V$_2$O$_8$ polycrystalline ceramic samples.

The Ni$_3$V$_2$O$_8$ thin films were fabricated from a phase pure nickel vanadate target. The Ni$_3$V$_2$O$_8$ powder used for the sputtering target was prepared by the solid state reaction
technique described above. Approximately 30 g of Ni$_3$V$_2$O$_8$ powder was mixed with 15 mL of 2 mole percent polyvinyl alcohol (PVA) as binder. The dried powder was pressed into a circular disc of approximately 50 mm diameter with thickness about 3.5 mm, using a 2 inch diameter die and hydraulic press at 2000 PSI. This compact disc was heat treated in air at 600 °C for 4 hours to burn off the binder organics and then finally sintered in air at 1000 °C for approximately 8 hours. Ni$_3$V$_2$O$_8$ thin films were fabricated onto (0001) c-sapphire and highly conducting (100) Si substrates. These pre-cleaned c-sapphire and Si substrates were mounted in the sputtering chamber and the chamber was evacuated and kept at the base pressure $\sim 10^{-6}$ torr using a cryo pump supported by normal rotary rough pump for more than $\sim 12$ hours to remove any residual gaseous impurities. The Ni$_3$V$_2$O$_8$ thin films were deposited at room temperature for 4 hours using a mixture of argon (Ar) as a sputtering gas and oxygen (O$_2$) as a reactive gas at $1.35 \times 10^{-2}$ torr and $1.5 \times 10^{-3}$ torr respectively with total working pressure maintained at $\sim 1.5 \times 10^{-2}$ torr inside the sputtering chamber. The as prepared thin films on both sapphire and Si substrates were amorphous and were annealed in air at 1000 °C for 1 hours to get single phase Ni$_3$V$_2$O$_8$ thin films.

6.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF Ni$_3$V$_2$O$_8$ THIN FILMS

The structural properties of Ni$_3$V$_2$O$_8$ thin films were investigated using Rigaku RU2000 powder X-ray diffractometer. The room temperature $\theta - 2\theta$ X-ray diffraction patterns for Ni$_3$V$_2$O$_8$ thin films fabricated on c-axis sapphire and (100) silicon substrates are shown in Fig 6.2. In contrast to the diffuse background for as deposited amorphous Ni$_3$V$_2$O$_8$ thin films, the high temperature air annealed Ni$_3$V$_2$O$_8$ films are highly textured along the b-axis for both sapphire and silicon substrates, although they remain polycrystalline, as shown in Fig 6.2. All the diffraction peaks can be indexed to the Ni$_3$V$_2$O$_8$ orthorhombic crystal structure (JCPDS no. 70-1394), suggesting that no impurity phases are present.
Figure 6.2: The $\theta - 2\theta$ XRD pattern for $\text{Ni}_3\text{V}_2\text{O}_8$ thin films on (0001) sapphire (top panel) and n-type conducting (100) silicon (lower panel)
The surface and cross-sectional microstructural investigation of these rf sputtered Ni$_3$V$_2$O$_8$ thin films were carried out using scanning electron microscopy. The surface SEM micrographs shows that these films have numerous structural defects, including pinholes, as shown in Fig 6.3. The cross-sectional micrograph, shown in inset in Fig 6.3, was used to study the interface quality and film thickness. The calculated thickness for these films is $\sim$500 nm and the film interface is not very sharply defined. The associated EDX accessory on the SEM was used to estimate the ratio of Ni and V, which was found to follow the correct stoichiometric atomic ratio of Ni:V (3:2). To further probe the lattice structure and look for possible secondary phases, we conducted room temperature Raman vibrational spectroscopic measurements using a Horiba Triax Raman spectrometer. The Raman spectra for Ni$_3$V$_2$O$_8$ thin films is shown in Fig 6.4 (bottom panel) and is in good agreement with Ni$_3$V$_2$O$_8$ single crystal Raman spectrum, shown in Fig 6.4 (top panel) for comparison, indicating that these Ni$_3$V$_2$O$_8$ thin films are highly crystalline without any secondary phases.

The primitive unit cell of Ni$_3$V$_2$O$_8$ contains 26 atoms, which lead to the possible $26\times3=78$ independent atomic displacements. The $\Gamma_v$ representation induced by the vector space of these 78 atomic displacements decomposes as:

$$
\Gamma_v = 10A_g + 8A_u + 8B_{1g} + 13B_{1u} + 7B_{2g} + 12B_{2u} + 11B_{3g} + 9B_{3u} \quad (6.4)
$$

The vector representations that transform along x, y and z are the $B_{3u}$, $B_{2u}$ and $B_{1u}$ symmetry modes respectively and these are the only modes responsible for IR activity [191]. The ferroelectric polarization in Ni$_3$V$_2$O$_8$ must result from the condensation of one or more of the twelve $B_{2u}$ symmetry modes, as symmetry restricts polarization along b-axis in this system.

The measured Raman spectrum is similar to the spectrum obtained for the phonon density of states using inelastic neutron scattering and can be divided into three well separated energy regions. The first region falls between 15-60 meV ($\sim$121-484 cm$^{-1}$) and is due to ro-
Figure 6.3: The representative surface SEM micrograph, with inset showing cross-sectional SEM image for Ni$_3$V$_2$O$_8$/Sap thin film

tations/translations (low energy portion) and small distortions of the NiO$_6$ octahedra (high energy portion). The second phonon region falls in 75-85 meV ($\sim$ 605-686 cm$^{-1}$). It includes mainly the vibration of the O(2) along the V-O bond. Since all oxygen are atoms are connected to the Ni atoms, these modes cannot be described as purely V-O bond stretching because they always have some Ni-O bond stretching as well. The third phonon region fall in the energy range 90-105 meV ($\sim$ 726-847 cm$^{-1}$). These modes are very similar to the second region, that is, oxygen vibration along the V-O bond, but they are also mixed with O-Ni-O bending and therefore occurs at higher energies.

Spin-phonon coupling mediated by the 80 meV (=645.28 cm$^{-1}$) vibrational mode has been proposed as a possible mechanism for the magnetically induced ferroelectricity in Ni$_3$V$_2$O$_8$ [191]. The most striking feature observed in the Raman spectrum is that the peak associated to 80 meV has been split into two separate peaks for both single crystal and thin film Ni$_3$V$_2$O$_8$ samples in contrast to the single peak observed in inelastic neutron scattering at same energy.
Figure 6.4: The room temperature Raman spectrum for a Ni$_3$V$_2$O$_8$/Sap thin film (bottom panel) and a Ni$_3$V$_2$O$_8$ single crystal (top panel)

This splitting may provide some insight into the specific mechanisms responsible for onset of ferroelectricity in this system.

### 6.2.3 COMPOSITION, OPTICAL AND ELECTRONIC PROPERTIES

To probe the chemical valence states for constituent elements of Ni$_3$V$_2$O$_8$ we conducted X-ray photoelectron spectroscopy (XPS) measurements on Ni$_3$V$_2$O$_8$ single crystals and Ni$_3$V$_2$O$_8$/Si thin films. The narrow scan XPS spectra of nickel, vanadium and oxygen for Ni$_3$V$_2$O$_8$/Si thin film are plotted in Fig 6.5 (a) and (b). The XPS elemental Ni2P spectrum consists of 2P$_{3/2}$ and 2P$_{1/2}$ peaks, fall at binding energies of 855.86 eV and 873.68 eV respectively, as shown in Fig 6.5(a) and is similar to the Ni spectrum in octahedral configuration. The strong Ni satellite peak at 862.21 eV and the spin orbit splitting energy $\Delta$ Ni2P between the 2P$_{3/2}$ and 2P$_{1/2}$ peaks is 17.84 eV, confirming the 2+ valence state of Ni in this
compound. These high binding energies for Ni and the satellite peak also suggest that the electronic states of the ligand anion (in our case oxygen) contribute to the Ni2P binding energy of Ni in insulating state [192], which is consistent with the highly insulating nature of Ni$_3$V$_2$O$_8$. The vanadium 2P doublet is shown in Fig. 6.5(b), and consists of V2P$_{3/2}$ and V2P$_{1/2}$ at 516.9 eV and 524.04 eV respectively.

The spin-orbit splitting for V2P doublet is $\sim$7.14 eV, comparable to the theoretically predicted $\Delta$ V2P of 7.5 eV for V$_2$O$_5$, suggesting a 5+ valence state for vanadium, as expected in this sample. The narrow scan O1s XPS spectrum is shown in Fig. 6.5(b) together with vanadium spectrum, consists of O1s peak at $\sim$530.5 eV, which is consistent with a 2+ valence state. The compositional ratio for elements Ni, V and O in the Ni$_3$V$_2$O$_8$ films was determined using the expression $C_x = \frac{A_x/S_x}{\sum_x A_x/S_x}$, where C is the atomic concentration, x is the element under consideration, $A_x$ and $S_x$ are the area under the narrow scan curve and the sensitivity factor for element $x$ respectively. The sensitivity factors for Ni, V and O, used in calculating corresponding $C_x$ are 5.4, 1.4 and 0.63 respectively [193]. After correcting for an appropriate
Figure 6.6: The optical absorption \((\alpha * E)^2\) (left axis) and \((\alpha * E)^{1/2}\) (right axis) versus energy \(E\) for \(\text{Ni}_3\text{V}_2\text{O}_8/\text{Sap}\) thin films. The inset showing \((\alpha * E)^2\) versus energy \(E\) plot, exhibiting a strong absorption \(\sim 1.3\) eV, indicating an Ni d-d interband transition as schematically shown in the representative energy band diagram.

Shirley-type background, we used the estimated \(A_x\) for \(\text{Ni}_2\text{P}_{3/2}\), \(\text{V}_2\text{P}_{3/2}\) and O1s and the respective \(S_x\), the estimated atomic percent ratio for Ni:V:O is \(\sim 23\% : 15\% : 62\%\). Within our uncertainties, the Ni to V atomic ratio is 3:2, consistent with our EDX microanalysis of the \(\text{Ni}_3\text{V}_2\text{O}_8\) thin film samples, indicating the correct stoichiometry for \(\text{Ni}_3\text{V}_2\text{O}_8\) thin films.

To investigate the electronic structure of \(\text{Ni}_3\text{V}_2\text{O}_8\) system, we measured the optical transmittance and reflectance from 175 nm to 3300 nm for \(\text{Ni}_3\text{V}_2\text{O}_8/\text{Sap}\) thin films. The well defined interference fringes from the reflection spectrum were used to estimate the film thickness, which is in good agreement with values estimated from cross-sectional SEM images for these samples.

We plot \((\alpha * E)^2\) versus energy \(E\) in Fig 6.6 for the \(\text{Ni}_3\text{V}_2\text{O}_8/\text{Sap}\) thin films. A sharp linear region above the optical band edge absorption suggests that \(\text{Ni}_3\text{V}_2\text{O}_8\) is a direct band gap system. The extrapolation of the higher energy linear region of \((\alpha * E)^2\) to \(E=0\) gives a band gap of \(E_g \sim 2.2\) eV. Additionally we also plot \((\alpha * E)^{1/2}\) versus energy \(E\) in Fig 6.6 , which does not exhibit any clear bandgap absorption. This eliminates the possibility of an
indirect bandgap in $\text{Ni}_3\text{V}_2\text{O}_8$. More interestingly we observe an additional broad, but still strong, absorption feature at $\sim 1.3$ eV. This feature may be mainly ascribed to d-d electron transitions between the split Ni 3d orbitals in the octahedral field [194].

We plot the valence band (VB) XPS spectrum for $\text{Ni}_3\text{V}_2\text{O}_8$/Si thin film samples in the top panel of Fig 6.7. The energy of the uppermost valence band with respect to the Fermi energy $E_F$ is determined by extrapolating the leading edge of the valence band spectrum to the base line and is estimated as $\sim 1.1$ eV. These results are close to the those obtained on $\text{Ni}_3\text{V}_2\text{O}_8$/Sap thin film and single crystal samples. Based on the VB XPS spectrum and the measured optical bandgap $E_g$, we find that the Fermi energy $E_F$ lies approximately in between the conduction band minimum and valence band maximum, explaining the intrinsic insulating behaviour of this material. A schematic band diagram for $\text{Ni}_3\text{V}_2\text{O}_8$ is shown as an inset at the left top in Fig 6.6, with the possible Ni d-d transitions. The Ni3d split orbitals, the occupied $(t_{2g} + b_{1g})$ states and the empty $b_{2g}$ state, in the octahedral crystal field are supposed to play a crucial role in determining the electronic structure [195]. The conduction
band of Ni$_3$V$_2$O$_8$ is composed of empty Ni3d orbitals and valence band is composed of O2p and the occupied V3d orbitals (the $e$ state in a tetrahedral field). The electronic transition from O2p to the empty Ni3d $b_{2g}$ orbitals accounts for the measured optical band gap $\sim$2.2 eV, whiles transitions from the occupied Ni3d ($t_{2g} + b_{1g}$) orbitals to the empty Ni3d $b_{2g}$ orbitals correspond to the observed d-d electron transition between the split Ni3d orbitals in the octahedral field [196].

These studies suggests that Ni$_3$V$_2$O$_8$ is an insulating magnetic material with optical energy bandgap $E_g \sim$2.2 eV and that the Fermi level ($E_F$) lies nearly at the middle of bandgap. Furthermore, we also observed additional Ni d-d interband transitions. The complex electronic structure with interband Ni d-d transitions may have an important role in the spin-phonon coupling and hence development of ferroelectric and magnetic ordering simultaneously near the LTI ($\sim$6.4 K) magnetic phase.

### 6.2.4 ELECTRIC AND MAGNETIC FIELD CONTROL OF MULTIFERROIC TRANSITION IN Ni$_3$V$_2$O$_8$ SYSTEM

Magnetoelectric multiferroics exhibit the cross-control of magnetic and ferroelectric order parameters. Motivated by this general statement we have investigated the electric field control of the multiferroic transition in Ni$_3$V$_2$O$_8$. The dielectric and magnetodielectric properties of Ni$_3$V$_2$O$_8$ single crystal are widely studied [70, 186, 190]. However, it is difficult to apply large electric field across a single crystal, as these have a thickness of approximately 1 mm, prompting this study to be undertaken on thin film samples. To probe the electric field control of the LTI magnetic phase, which is the only multiferroic phase, we used temperature, magnetic, and electric field dependent dielectric spectroscopy. All dielectric measurements were conducted using a 30 kHz excitation frequency near the LTI-HTI phase boundary at zero and finite applied electric and magnetic fields on Ni$_3$V$_2$O$_8$/Si thin films. The temperature dependence of the dielectric constant measured at zero bias voltage ($E=0$)
and applied magnetic field \((H=0)\) is shown in the bottom panel in Fig 6.8 (a). We observe a sharp dielectric peak at the HTI to LTI magnetic phase boundary i.e. \(\sim 6.4 \, \text{K}\) and we do not see any dielectric anomaly associated with other phase boundaries such as LTI-CAF at \(\sim 4 \, \text{K}\) and paramagnetic to HTI phase at \(\sim 9.1 \, \text{K}\). These results are consistent with bulk \(\text{Ni}_3\text{V}_2\text{O}_8\) ceramic and single crystal samples except at 4 K [70], where single crystal dielectric measurements show a large drop in dielectric constant at LTI-CAF phase boundary [186]. These dielectric measurements confirmed that \(\text{Ni}_3\text{V}_2\text{O}_8\) thin films are multiferroic in nature.

Further we conducted temperature dependent dielectric measurements under applied external electric and magnetic fields, both applied perpendicular to the film surface, along the b-axis of the \(\text{Ni}_3\text{V}_2\text{O}_8/\text{Si}\) thin films. These results are plotted in Fig 6.8(a) under different representative external electric and magnetic fields. The dielectric anomaly associated with the LTI magnetic transition, shifts up by \(\Delta T \sim 0.2K \pm 0.05K\), when an electric field of \(E=25 \, \text{MV/m}\) is applied. We also measured the \(\text{Ni}_3\text{V}_2\text{O}_8\) dielectric constant under the simultaneously applied electric (\(E=25 \, \text{MV/m}\)) and magnetic (\(\mu H=7.5 \, \text{T}\)) fields. The single dielectric peak, indicating the development of the LTI magnetic structure, shifts down in the temperature by 0.4 K, which rules out the possibility that the magnetic and ferroelectric phase transitions split in finite electric field. This suggest that the multiferroic transition \(\sim 6.4\text{K}\) is sensitive to both magnetic and electric fields.

The electric and magnetic field dependence of the multiferroic transition \(T_L \sim 6.4K\), that is, the HTI-LTI phase boundary, is shown in Fig 6.8(b). This curve is built from transition values extracted from different applied electric and magnetic field measurements. These magnetic field dependent measurements were collected at zero electric field and electric field dependent measurements were collected at zero magnetic field. The applied bias voltage increases the transition temperature non-linearly, while an applied magnetic field lowers the transition temperature non-linearly, as shown in Fig 6.8(b). The phase boundaries can be fit to power law behaviour. The magnetic phase boundary follows a quadratic field dependence.
Figure 6.8: (a) Dielectric constant versus temperature at $E = 0 = \mu_0 H$ fields (bottom panel) and $E=25$ MV/m, $\mu_0 H=0$ T (middle panel) and $E=25$ MV/m, $\mu_0 H=8$ T (top panel) for Ni$_3$V$_2$O$_8$/Si thin film and (b) E-H-T phase diagram for Ni$_3$V$_2$O$_8$ near the HTI to LTI phase transition, where red triangles and blue circles represent the variation of $T_L$ with magnetic and electric fields with solid lines showing power law fits to the magnetic and electric field variation of $T_L$.

as $H \sim |T_L - T_{L0}|^{0.4}$, where $T_L$ is the transition temperature at magnetic field $H$ and $T_{L0}$ is the transition temperature at zero magnetic field. This is in agreement with the predictions that the HTI-LTI phase boundary should scale with magnetic field as $T_L(H) \sim T_{L0} - AH^2$, where $H$ is a non-critical field for the LTI order parameter and $A$ is the constant. The electric field-temperature (E-T) phase boundary exhibit a functional form given by $E \sim (T - T_L)^{2.4}$. This electric field dependence of the HTI-LTI phase boundary can be explained within the framework of a mean field trilinear coupling between the LTI and HTI magnetic order parameters and the spontaneous polarization [189]. This model predicts the onset of ferroelectric order associated with the magnetic structure in the LTI phase and also predicts that inducing a polarization by applying electric field should stabilize the LTI magnetic structure. The free energy near the LTI-HTI phase boundary is given by:
\[
F = \frac{P^2}{2\chi_E} + ia(\langle\sigma_{HTI}\rangle\sigma_{LTI} - \langle\sigma_{HTI}\rangle\sigma_{LTI}^*)P_b + \frac{1}{2}(T - T_L)|\sigma_{LTI}|^2 - \vec{E} \cdot \vec{P} \quad (6.5)
\]

where \(\chi_E\) is electric susceptibility and \(a\) is a constant. Since the LTI-HTI phase boundary is far from the transition to HTI phase, the HTI magnetic order parameter \(\sigma_{HTI}\) is replaced by its average value \(\langle\sigma_{HTI}\rangle\). Diagonalizing the quadratic form in \(P_b\) and \(\sigma_{LTI}\), we get the true LTI order parameter, \(\tilde{\sigma}\), which is given by:

\[
\tilde{\sigma} = b\sigma_{LTI} + b^*\sigma_{LTI}^* + cP_b \quad (6.6)
\]

This equation explains that an applied electric field acts as a field conjugate to the real order parameter \(\tilde{\sigma}\). Near the HTI - LTI phase boundary the order parameter can be given as:

\[
\langle\tilde{\sigma}\rangle = t^\beta F(E^{-\beta-\gamma}) \quad (6.7)
\]

where \(F\) is an unknown scaling function, \(\beta\) and \(\gamma\) are the critical exponents for the magnetization and susceptibility respectively. Thus, the electric field variation of the HTI - LTI phase boundary is predicted to follow \(E \sim \Delta T^{\beta+\gamma}\). Within the mean field approximation the values of \(\beta\) and \(\gamma\) are 1/2 and 1 respectively, leading to \(E \sim \Delta T^{1.5}\). However, critical fluctuations will lead to a significant increase in \(\gamma\) and a smaller decrease in \(\beta\), leading to \(\beta + \gamma \sim 1.7\) or more. This is lower than the power exponent 2.4 estimated from the fit, as shown in Fig 6.8 (b), but this mean field model still provides a qualitative explanation for the nature of \(E - T\) phase boundary curve.

We find that the temperature for a magnetic phase transition in \(\text{Ni}_3\text{V}_2\text{O}_8\) thin films can be controlled by an external electric field. The application of an electric field stabilizes the \(\text{Ni}_3\text{V}_2\text{O}_8\) LTI phase due to the coupling of magnetic and ferroelectric order parameters.
Additionally, we observe that the low field phase boundaries for the HTI-LTI multiferroic phase transition in Ni$_3$V$_2$O$_8$ are consistent with power law scaling.

6.2.5 DIELECTRIC CRITICAL BEHAVIOUR AT MULTIFERROIC TRANSITION TEMPERATURE FOR Ni$_3$V$_2$O$_8$ SYSTEM

Nickel vandate Ni$_3$V$_2$O$_8$ exhibits a distinct dielectric anomaly at multiferroic transition $T_L$=6.4 K associated with the transition to the ferroelectrically ordered LTI state [70]. The divergence of the dielectric constant at a phase transition (in our case the multiferroic transition) can be understood in the framework of critical behaviour, where the dielectric constant is described by function of the form:

$$
\epsilon = \Gamma^+ |t|^{-\gamma^+} + B + Ct
$$

where $|t|$ is the magnitude of the reduced temperature, $|t| = |(T - T_C)/T_C|$, $\Gamma^\pm$ are the amplitudes above and below the transition temperature, $\gamma^\pm$ are the critical exponents above and below the transition temperature, and $B+Ct$ is the non-critical background. The scaling hypothesis predicts that $\gamma^+ = \gamma^- = \gamma$, but that the amplitudes $\Gamma^+$ and $\Gamma^-$ will differ. The critical exponent $\gamma$ and ratio $\Gamma^+ / \Gamma^-$ are found to depend on the universality class of the system.

We measured the dielectric response of single crystal Ni$_3$V$_2$O$_8$ for temperatures very close to $T_L$ to analyze the critical scaling of dielectric constant at $T_L$ and to investigate the universality class for the multiferroic transition. The dielectric measurements of Ni$_3$V$_2$O$_8$ single crystal were carried out in parallel plate capacitor geometry using Au electrodes as top and bottom electrodes and Cu wires were attached using silver epoxy as the conducting leads. We measured the dielectric constant using an 4284A Agilent LCR meter in conjunction with...
Figure 6.9: (a) Temperature dependence of the dielectric constant near multiferroic transition temperature $T_L$ of a Ni$_3$V$_2$O$_8$ single crystal, where the solid lines are fits to critical behaviour (b) Relative change in the dielectric constant of a Ni$_3$V$_2$O$_8$ single crystal versus reduced temperature $|t|$ at three different warming rates 0.1K/min (squares), 0.05K/min (triangles) and 0.01K/min (circles). The solid symbols indicate data above $T_L$ while open symbols indicate data below $T_L$. The dashed lines show the fits to critical behaviour.

Quantum Design PPMS temperature control option, where electric field electric field was applied along the b-axis of the Ni$_3$V$_2$O$_8$ single crystal. The dielectric measurements were carried out on slowly warming and cooling through the phase transition at different rates and different measuring frequencies. There was no difference between measurements taken on warming or cooling, showing that the rate of temperature change was small enough to avoid significant thermal lag between the sample and thermometer.

The temperature dependent dielectric constant for Ni$_3$V$_2$O$_8$, measured at 30 kHz while warming at 0.01 K/min, is shown in Fig 6.9 (a), where the solid lines showing the best fit to Eq. (6.8), requiring different values for $\gamma^+$ and $\gamma^-$. Above $T_L$, the best fit is obtained in the reduced temperature range $0.003 < -t- > 0.02$. There is some dependence of $\gamma^{pm}$ on the fitting range, value of $T_L$ used and background correction term, but we consistently find that $\gamma^- > \gamma^+$. Although the functional form of the dielectric constant described by Eq. (6.8) explains the essential behaviour of $\epsilon$ over some range of temperature close to $T_L$, the dielectric constant of Ni$_3$V$_2$O$_8$ diverges from this expression for small $t$. This divergence, close to $|t| = 0.002$ can be attributed to Gaussian smearing of $T_L$ associated with inhomogeneities in the sample [197].
The relative change in the dielectric constant versus reduced temperature for Ni$_3$V$_2$O$_8$ is shown on a log-log plot in Fig 6.9 (b). The open symbols are for T < T$_L$ and solid symbols show the data for T > T$_L$. We also conducted measurements at different warming rates to examine its effect on dielectric constant. As shown in Fig 6.9 (b), the dielectric constant near T$_L$ is invariant when the warming rate is changed by an order of magnitude, ruling out any possibility of poor thermal equilibrium during measurements. The black dashed line shows the best fit of the divergent dielectric constant to $\Gamma^+ |t|^{-\gamma^+}$ with $\gamma^+ = 1.6$, while the gray dashed line shows the best fit to $\Gamma^- |t|^{-\gamma^-}$ with $\gamma^- = 2.5$. In addition to different values for $\gamma$ above and below $T_L$, the ratio $\Gamma^+/\Gamma^-$ determined from the fits shown in Fig 6.9 (b) is almost two orders of magnitude larger than typical values (which are on the order of 1) [198].

Different critical exponents above and below $T_c$ have also been observed in other systems such as YMnO$_3$ [184] and different explanations have been suggested for this discrepancy. The presence of different order parameters and coupling between these, as is present in multiferroics, may modify the corresponding phase diagram and hence scaling fields, leading to different critical exponents above and below $T_c$.

### 6.3 CONCLUSION

We have studied the electronic, optical, and magneto-electronic properties of Ni$_3$V$_2$O$_8$ in bulk and thin film geometries. Our results suggest that Ni$_3$V$_2$O$_8$ is a direct bandgap magneto-electric multiferroic with $E_g \sim 2.2$ eV with a Fermi energy lying in the middle of the optical bandgap. This suggests that Ni$_3$V$_2$O$_8$ is a magnetic insulator, an essential condition for ferroelectric materials, exhibiting strong magneto-electric coupling. Additionally our measurements on the temperature dependence of the dielectric constant in thin films samples at different electric and magnetic field suggest that multiferroic transition can be cross controlled by both electric and magnetic field. This confirms the the strong magneto-electric
coupling between magnetic and ferroic order parameters. Such cross control of magnetic and ferroelectric order parameters may provide a mechanism for four state memory devices. We have also investigated the critical behaviour at the LTI transition in Ni$_3$V$_2$O$_8$. These studies suggest that critical exponent differs above and below $T_c$. 
Chapter 7

FeVO$_4$ MULTIFERROIC - A NEW MULTIFERROIC IN VANADATE FAMILY

7.1 INTRODUCTION

Among the various transition metal vanadates having general formula TM$_3$V$_2$O$_8$, where TM is a magnetic transition metal (Cu, Ni, Co or Mn) and V is a non-magnetic ion, Ni$_3$V$_2$O$_8$ is the only system identified as a multiferroic. A closely related iron vanadate, FeVO$_4$, has recently been identified as a multiferroic system [71, 199], and has a number of similarities with Ni$_3$V$_2$O$_8$. This system crystallizes into a triclinic structure with $P\bar{1}$ space group and $C_i$ point group, containing a chain structure built from Fe-O polyhedral. In this material, the spin 5/2 Fe$^{3+}$ ions have three distinct crystallographic sites separated by (VO$_4$)$^{3-}$ groups containing non-magnetic V$^{3+}$ ions [200], as shown in Fig 6.10. This is the only stable phase at ambient conditions among other metastable phases, which are usually formed at high pressure and high temperature conditions [201].

This compound shows two distinct antiferromagnetic transitions at $T_{N1} \sim 22K$ and
Figure 7.1: (a) The chain structure of FeVO$_4$ consist of Fe-O polyhedra and (b) the form of a six-column doubly bent chain

$T_{N2} \sim 15K$ [71]. Neutron studies on single crystal FeVO$_4$ [199], have found that magnetic structure below $T_{N2}$ is non-collinear and incommensurate, while between $T_{N1}$ and $T_{N2}$, the magnetic structure is collinear and incommensurate. This system exhibits the onset of ferroelectricity below the spiral magnetic transition at $T_{N2}$[71].

In this section we will discuss the synthesis of FeVO$_4$ ceramic and thin films, magnetic structure, room temperature optical and electronic properties, the onset of ferroelectricity at an antiferromagnetic transition and magnetoelectric coupling in both bulk and thin film geometries.

### 7.2 EXPERIMENTS AND RESULTS
7.2.1 SYNTHESIS OF FeVO$_4$ BULK CERAMIC AND THIN FILM SAMPLES

The bulk FeVO$_4$ ceramic samples were prepared using metal organic solution and standard solid state reaction technique, described in detail in Appendix B 1. Motivated by the goal of synthesizing Fe$_3$V$_2$O$_8$, a structural analog of multiferroic Ni$_3$V$_2$O$_8$, we prepared a homogeneous mixture of iron (II)-2 ethylhexanoate and vanadium naphthenate solutions having Fe to V atomic ratio of 3:2. This attempt to make Fe$_3$V$_2$O$_8$ was unsuccessful, but our synthesis unexpectedly produced single phase FeVO$_4$ iron vanadate. This homogeneous mixture was heated slowly to 350 °C for 2 hours to burn off the organics from the metal organic solution. The resulting black powder was calcinated in air at 800 °C for 2-4 hours, yielding a yellowish brown powder, identified as a single phase FeO$_4$. We observed that a small amount of material spilled out of the crucible during the high temperature sintering step due to the thermal agitation, possibly leading to the stoichiometric FeVO$_4$ remaining in the crucible. Later we repeated the synthesis of single phase FeVO$_4$ starting from a homogeneous mixture of iron (II)-2 ethylhexanoate and vanadium naphthenate solution in the desired 1:1 atomic ratio of Fe:V as the starting material followed by the same heat treatment. In addition to this metal organic solution synthesis, we also prepared ceramic FeVO$_4$ samples using a solid state reaction technique. A stoichiometric ratio of iron oxide (Fe$_2$O$_3$) and vanadium pentaoxide (V$_2$O$_5$) solid solutions were thoroughly mixed and grounded to homogenize the mixture. This mixture was slowly heated to 600 °C for 4 hours in air. This process was repeated 3-4 times to complete the solid state reaction. This homogeneous solid solution was finally heated in air at 800 °C for 4 hours, to get single phase FeVO$_4$.

The FeVO$_4$ thin films were prepared on single crystal (0001) c-sapphire (Al$_2$O$_3$) and highly conducting n type (100) conducting silicon (Si) substrates using RF magnetron sputtering. The iron vanadate sputtering target was prepared using the FeVO$_4$ phase pure powder, which was prepared using the solid state reaction described above. Approximately
30g of FeVO$_4$ powder was mixed thoroughly with 15 mL of 2 mole percent polyvinyl alcohol (PVA) in deionized water as a binder. The dried powder was pressed into approximately 50 mm diameter circular disc with a thickness of $\sim$3.5 mm using 2 inch die and a hydraulic press at 2000 PSI. This circular disc serving as the sputtering target was heated in air at 600 °C for 4 hours to burn off organics, followed by a final sintering at 800 °C for 4 hours to produce a dense compact pellet. The cleaned sapphire and conducting Si substrates were mounted and the sputtering chamber was evacuated to a base pressure of $10^{-6}$ torr using a cryo pump and left under vacuum for more than $\sim$12 hours to remove any residual gaseous impurities/leftovers. The FeVO$_4$ thin films were deposited at room temperature for 4 hours by sputtering stoichiometric phase pure iron vanadate target using the mixture of sputtering gas argon (Ar) and reactive gas oxygen (O$_2$) at $1.35 \times 10^{-2}$ torr and $1.5 \times 10^{-3}$ torr respectively with total working pressure at $1.5 \times 10^{-2}$ torr inside the sputtering chamber. The as prepared thin films on both sapphire and Si substrates were amorphous and were annealed in air at 700 °C for 4 hours to get single phase FeVO$_4$ thin films.

7.2.2 STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF BULK AND THIN FILM FeVO$_4$ SAMPLES

The structural indentification of bulk ceramic and thin film FeVO$_4$ samples was carried out using X-ray diffraction. The $\theta - 2\theta$ powder XRD pattern was collected at room temperature and is shown in Fig 6.11. The peaks from polycrystalline bulk and thin film FeVO$_4$ samples can be completely indexed to the triclinic FeVO$_4$ structure (JCPDF # 38-1372). We do not observe any secondary phases such as iron oxide for these samples. However, these XRD studies are not sufficiently precise to rule out the possibility of an amorphous impurity or few volume percent of a secondary phase.

The microstructural characterization of FeVO$_4$ thin film was carried out using a scanning electron microscope (SEM). The surface micrograph is shown in Fig 6.12(a), which indicates
Figure 7.2: XRD ($\theta - 2\theta$) pattern for (a) FeVO$_4$ bulk powder, where the expected peak positions are indicated by dashed lines (red) along the lower edge of figure. (b) FeVO$_4$ thin film
that the thin film consists of grains with various orientations as well as a number of pinhole defects. The cross-sectional SEM is also shown as in Fig 6.12(b), indicating sharp interface with the substrate and thickness $\sim 200$ nm.

We have used Raman spectroscopy, which is very sensitive to the presence of impurities or secondary phases in the system, to further investigate the microstructure of iron vanadate samples. The room temperature Raman vibrational spectrum of iron vanadate for bulk and thin film geometries are shown in Fig 6.12(c). The FeVO$_4$ unit cell contains a total of 36 atoms consisting of 3 symmetry inequivalent VO$_4$ tetrahedra, two symmetry inequivalent FeO$_6$ octahedra and one FeO$_5$ polyhedra [202]. The point group for iron vanadate is $C_i$, leading to 54 Raman active optical modes belonging to the $A_g$ irreducible representation, with the remaining 51 IR active optical modes belong to $A_u$. We identify a total of 29 Raman active modes for both iron vanadate bulk ceramic and thin film samples. These room temperature Raman studies are in good agreement with a previously measured Raman spectrum on this sample [203], supporting the XRD results of absence of possible secondary phases or amorphous impurities.
7.2.3 ELEMENTAL, ELECTRONIC AND OPTICAL PROPERTIES

The valence states of the Fe and V cations play a central role in determining the electronic properties of FeVO₄, along with affecting the magnetic structure and, possibly, the magnetoelectric coupling. We studied the elemental and valence band structure of the FeVO₄ ceramic and thin film samples using a Perkins Elmer XPS system. The narrow scan XPS spectra of iron, vanadium, and oxygen for the ceramic sample are plotted in Fig 6.13. The pure Fe 2P doublet consists of 2P₃/₂, which shows a peak at 711.4eV, and 2P₁/₂, with a peak at 724.7eV, are ascribed to Fe2P₃/₂-O and Fe2P₁/₂-O bonds confirming the 3+ valence state for Fe. The spin-orbit splitting for the pure Fe2P doublet is roughly 13.3 eV, comparable to the reference value for Fe2P of 13.6 eV for Fe₂O₃ [193], consistent with a 3+ iron valence state in FeVO₄.
The elemental Fe spectrum (Fig 6.13 (top panel)) does not show evidence for any Fe in
the 2+ valence state, which is usually seen at lower binding energy, confirming the phase
purity of the sample. The vanadium 2P doublet, shown in Fig 6.13 (lower panel), consists of
V2P$_{3/2}$ and V2P$_{1/2}$ at 517.1 eV and 524.2 eV respectively. The spin-orbit splitting for the
V2P doublet is $\sim$7.1 eV, in line with the theoretically predicted value for V2P of 7.5 eV for
V$_2$O$_5$, confirming the 5+ valence state for vanadium. The narrow scan O1s XPS spectrum
is shown in Fig 6.13 (lower panel) in conjunction with the V XPS spectrum consists of O1s
peak at $\sim$530.5 eV, indicating that O is in the 2- valence state in FeVO$_4$. The elemental
composition was estimated determined using the expression $C_x = \frac{A_x}{S_x} \sum_x \frac{A_x}{S_x}$, where C is the
atomic concentration, x is the element under investigation, $A_x$ and $S_x$ are the area under the
narrow scan curve and the sensitivity factor for the element x respectively. The sensitivity
factors for Fe, V and O are 3.8, 1.4 and 0.63 respectively [193]. After and appropriate
Shirley-type background correction (not shown), we used the estimated area $A_x$ under the
Fe2P$_{3/2}$, V2P$_{3/2}$ and O1s peaks and corresponding sensitivity factor $S_x$, to find the atomic
percent ratio. The calculated atomic percent ration for Fe: V: O is 17.7%: 18.1%: 64.2%.
Within experimental error, the Fe to V ratio is 1:1, consistent with our EDX microanalysis.

Mapping the electronic structure using optical measurements has helped to clarify the
properties of a number of other multiferroic materials [204, 205]. We measured the optical
transmittance and reflectance between 175 nm and 3300 nm for the FeVO$_4$ thin films to
determine the absorbance and extract the absorption coefficient $\alpha = -ln(T(\lambda) + R(\lambda))/d$.
In this expression, $T(\lambda)$ and $R(\lambda)$ are the relative transmittance and reflectance at a given
wavelength $\lambda$ with $d$ the film thickness. We plot both $(\alpha * E)^2$ versus E, appropriate for
direct bandgap materials, and $(\alpha * E)^{1/2}$ versus E, suitable for indirect bandgap systems,
shown in Fig. 6.14.

The graph of $(\alpha * E)^2$ versus E can be fit by a straight line above the optical absorption
region, indicating that FeVO$_4$ is a direct band gap material. A linear extrapolation of $(\alpha*E)^2$
Figure 7.5: Optical absorption spectra \((\alpha * E)^{1/2}\) versus \(E\) (right axis) and \((\alpha * E)^2\) versus \(E\) (left axis) for \(\text{FeVO}_4/\text{Sap}\) thin films. The jump at 3.5 eV is due to the change in gratings at these wavelengths. The iron \(\text{Fe}^{3+}\) \((d^5)\) high spin electronic configuration in an octahedral coordination is shown in the inset.
to 0 gives an optical bandgap of 2.7 eV. Conversely, the \((\alpha \ast E)^{1/2}\) versus E plot does not exhibit clear sign of bandgap absorption edge, ruling out an indirect bandgap transition. The anomaly near 3.5 eV in the optical absorption spectrum is produced by a grating change in the spectrometer during the measurement.

Magnetic studies on FeVO\(_4\) suggest that iron is in the high spin \(d^5 (S = 5/2)\) configuration and is orbitally quenched, \(L = 0\) [206]. The high spin electronic configuration, promoted by the octahedral crystal field, is schematically shown as an inset in Fig 6.14, where the \(t_{2g}\) and \(e_g\) states are occupied at half filling. This high spin configuration is likely to suppress \(d-d\) transitions in FeVO\(_4\), which is consistent with the relatively linear behavior of \((\alpha \ast E)^2\) above the optical bandgap and the lack of any absorption features at lower energies. This should be contrasted with the optical response of multiferroic Ni\(_3\)V\(_2\)O\(_8\), which shows clear \(d-d\) transitions associated with electrons hopping between filled and half-filled \(d\) orbitals on the Ni\(^{2+}\) ions. Since these transitions are suppressed in the high spin, half filled Fe\(^{3+}\) \(d\)-orbitals in FeVO\(_4\), this iron vanadate may be preferable for testing theoretical models for the electronic structure in multiferroic materials.

We plot the valence band (VB) XPS spectrum for the FeVO\(_4\) ceramic sample in Fig 6.15. Extrapolating the leading edge of the valence band spectrum to zero, as indicated by the dashed line in Fig. 6.15, gives the energy of the uppermost valence band for FeVO\(_4\) system with respect to the Fermi energy \(E_F\). This falls at 1.35 eV, at the midpoint of the 2.7 eV bandgap extracted for FeVO\(_4\) using optical spectroscopy as discussed in the context of Fig 6.14. This result is consistent with the intrinsic insulating properties of FeVO\(_4\). A schematic band diagram for FeVO\(_4\) is included as an inset in Fig 6.15, showing the 2.7 eV bandgap between valence and conduction bands with the Fermi energy falling in the middle of gap.
7.2.4 MAGNETIC AND THERMAL PROPERTIES OF FeVO$_4$ BULK CERAMIC SAMPLES

The dc magnetic properties of FeVO$_4$ bulk system were investigated using a Quantum Design SQUID magnetometer. The temperature dependent magnetic susceptibility was measured at 100 Oe and is shown in Fig 6.16 (a), also showing the temperature dependence of the inverse susceptibility.

The low temperature (5 K-40 K) magnetic susceptibility measured at 100 Oe and 10 and 50 KOe is shown in Fig 6.16 (b). These magnetic measurements show two clear antiferromagnetic (AFM) transitions at $T_{N1} \sim 22$ K and $T_{N2} \sim 15$ K. The observed AFM transition at $T_{N1}$ indicates the onset of the higher temperature incommensurate magnetic order and that at $T_{N2}$ is associated with the development of the lower temperature incommensurate magnetic order. We fitted Curie-Weiss equation.
Figure 7.7: (a) Magnetic and inverse magnetic susceptibility versus temperature for a FeVO$_4$ bulk ceramic measured at 100 Oe, where the dashed line is the high temperature Curie-Weiss fit to the magnetic data. (b) Magnetic susceptibility at H=100 Oe, 10 kOe and 50 kOe.

\[
\chi = \frac{C}{T - \Theta_{CW}}
\]  

(7.1)

to the high temperature inverse magnetic susceptibility as shown in Fig 6.16 (a), where $\chi$ is the magnetic susceptibility, $C$ is the Curie-Weiss constant and $\Theta_{CW}$ is the Curie Weiss temperature. The calculated values of Curie-Weiss constant $C$ and Curie-Weiss temperature are 4.15 $\text{emuKmol}^{-1}$ and -126 K respectively. The relatively large $\Theta_{CW}$ compared to the ordering temperature indicates that there is some degree of magnetic frustration in this system, and allows considerable short-range magnetic correlations to develop above $T_N$. The frustration index $f = \frac{\Theta_{CW}}{T_N}$ is $\sim 5.7$, indicating a moderate degree of frustration. The effective magnetic moment in the paramagnetic phase, calculated from the the Curie constant $C$ is 5.54 $\mu_B$. This value of effective moment is in close agreement to the $\mu_{eff} = 5.92\mu_B$ for $S = 5/2$ Fe$^{3+}$ ions in their high spin configuration ($\mu_{L+S} = \sqrt{4S(S+1)+L(L+1)}$) with quenched iron orbital moments ($L = 0$). We also conducted dc magnetic measurements on
Figure 7.8: Temperature dependent heat capacity for FeVO$_4$ bulk ceramic at H=0 T plotted as: (a) C/T versus T and (b) C/T$^2$ versus T, where dashed line is the best fit at higher temperature to $C/T = \gamma T + \alpha T^3$.

FeVO$_4$ thin film samples and were unable to distinguish the very small magnetic anomalies associated with AFM transitions from the background in the thin film samples.

We have measured the specific heat capacity of bulk FeVO$_4$ using the standard relaxation technique on a Quantum Design PPMS. We mixed the FeVO$_4$ powder with silver powder in a 1:1 ratio then cold-pressed the composite into a solid pellet to ensure good internal thermal contact. The contribution from the silver powder was measured separately and subtracted to get the net FeVO$_4$ heat capacity contribution. The temperature dependent heat capacity C/T versus T and C/T versus $T^2$ plots are shown in Fig 6.17.

The heat capacity shows two lambda type anomalies at 22 K and 15 K, corresponding to the two magnetic phase transitions at $T_{N1}$ and $T_{N2}$ respectively. We fit the heat capacity data using $C = \gamma T + \beta T^3$ over the intermediate temperature range from T = 30 K to 50 K, as
shown in Fig 6.17 (b). Here $\gamma T$ is a magnetic contribution to the heat capacity from the spin ordering with in the system, as $FeVO_4$ is a good insulator and $\beta T^3$ is the lattice (phonon) contribution to the heat capacity. The values of $\beta$ and $\gamma$ were calculated from the heat capacity fit and are $0.35 \, J\,mol^{-1}K^{-1}$ and $2.2 \times 10^{-5} \, J\,mol^{-1}K^{-4}$ respectively. These values differ from those obtained on a single crystal $FeVO_4$ extracted over approximately the same high temperature range [199]. We calculated the effective Debye temperature $\Theta_{D_{eff}}$ which is $\sim 810$ K, using $\beta$ and is close to the value of $\Theta_{D_{eff}} = 773$ K extracted for single crystal over approximately same temperature range [200] but much larger than the $\Theta_{D_{eff}} = 385$ K used to estimate the lattice contribution to the specific heat in polycrystalline $FeVO_4$ samples [199]. This suggest that there may be a significant magnetic contribution to the higher temperature $T^3$ heat capacity term. The linear contribution $\gamma T$ is generally associated with charge carriers in the system and would normally be negligibly small for insulating samples. This non-zero $\gamma T$ term provides evidence for some additional magnetic contributions to the heat capacity. This linear contribution is similar to that observed in some other insulating magnets and attributed to the spin-glass or cluster-glass-like fluctuations [207].

7.2.5 DIELECTRIC AND FERROELECTRIC PROPERTIES

In order to probe the multiferroic behaviour of the $FeVO_4$ ceramic sample, we measured the dielectric constant and pyrocurrent using an Agilent 4284A Precision LCR meter and a Keithley 6517A high resistance electrometer respectively in combination with the Quantum Design PPMS, which was used for the temperature and magnetic field control. The temperature dependence of the dielectric constant is shown in Fig 6.18, measured at a frequency of 30 KHz and a driving voltage of 1 V.

The dielectric constant shows a sharp peak at $T_{N2}$, associated with the divergence of the dielectric susceptibility at the ferroelectric transition. The observed dielectric constant is $\sim 15.5$ and the corresponding loss $\tan \delta < 0.001$, indicating that $FeVO_4$ is a good dielectric.
Figure 7.9: Bulk FeVO$_4$ sample polarization at poling fields E=±200 kV/m and H=0 Oe and for E=+200 kV/m with magnetic fields of H=10, 30, and 50 kOe. Inset: temperature dependence of the dielectric constant measured at H=0 and 50 kOe.

The dielectric anomaly corresponds to a change of roughly 0.1% in the dielectric constant, which is relatively smaller than corresponding change of ~18% observed in Ni$_3$V$_2$O$_8$ single crystals but consistent with polycrystalline Ni$_3$V$_2$O$_8$ powder samples where change was ~0.2% [208]. This dielectric anomaly shows a shift to lower temperatures in the presence of magnetic field and we observe $\Delta T_{N2} = 0.5$ K in a field of H=50 kOe. For pyrocurrent measurements, the FeVO$_4$ bulk sample was poled at $\pm 358 kV m^{-1}$ well above the ferroelectric transition temperature ($T_{N2} = 15$ K) and then cooled to 8 K at H = 0T magnetic field. The pyrocurrent was measured during 4 K/min warming rate at zero bias. The spontaneous polarization of FeVO$_4$ was obtained by integrating pyrocurrent and is $\sim 6 \mu C m^{-2}$. We also measured the polarization of FeVO$_4$ powder sample under an applied magnetic field, as shown in Fig 6.18. In addition to slight shift in the transition temperature, also seen in the dielectric measurements, the magnitude of polarization is slightly suppressed in an applied field, decreasing by approximately 17% in a field of H = 50 KOe.
Motivated to understand the phonon mediated magnetoelectric coupling in FeVO$_4$ system, we carried out temperature dependent Raman studies. Representative Raman spectra for bulk FeVO$_4$ measured at different temperatures are shown in Fig 6.19. As mentioned previously, we observed 29 Raman active modes out of the possible 54 Raman active modes for iron vanadate system. The temperature dependence of these Raman vibrational modes can be divided into two classes.

The first class of Raman modes do not show any significant temperature dependence, beyond some small uniform softening on cooling, and typically fall at smaller Raman shifts. These modes occur at 104, 119, 214, 253, 270, 404, 449 and 473 cm$^{-1}$ and can be associated with bending modes and with vibrations of FeO$_x$ polyhedra [202]. The second class of modes shows systematic changes in the Raman shift in the temperature region between $T_{N1}$ and $T_{N2}$, corresponding to the collinear antiferromagnetic phase. These modes fall at larger Raman shifts and are associated with the stretching of V-O-Fe and Fe-O bonds and the bending of Fe-O-V and Fe-O-Fe complexes [202]. The relative change in the representative Raman modes at 498, 733, 842 and 928 cm$^{-1}$ with temperature is shown in Fig 6.19(b). This second set of Raman modes shows an abrupt relative increase of approximately 0.5% in Raman shift in the temperature interval between $T_{N1}$ and $T_{N2}$. At low temperature, below $T_{N2}$ and at high temperature, above $T_{N1}$ the peak positions for these modes are approximately constant, again neglecting a monotonic temperature dependent shift. We propose that exchange stric- tion in the collinear incommensurate magnetic phase can change the phonon frequencies by modifying the effective elastic constant leading to a slight increase in the Raman shift of these modes. Such change in the optical phonon modes associated with long range magnetic order has be observed and suggested in the context of magnetically induced changed in the low frequency dielectric constant [65]. In this situation, the polar displacement associated with the development of ferroelectricity would eliminate this magnetic exchange and thus restore the associated phonon mode frequencies to their original values. The fact that the
Figure 7.10: (a) Temperature dependent Raman spectra on FeVO$_4$ bulk ceramic. (b) % relative change of Raman shifts for the 498, 733, 842 and 928 cm$^{-1}$ modes with temperature.
same Raman spectra is observed in both the low and high temperature iron vanadate phases suggests that the development of the ferroelectric phase does not significantly change the normal vibrations in the system despite the very small shifts in ion position that accompany a finite ferroelectric order.

To further probe the magnetodielectric coupling in iron vanadate system, we carried out temperature dependence of dielectric constant and resistivity for FeVO$_4$ bulk over a wide temperature range at 30KHz excitation frequency and H = 0T magnetic field, as shown in Fig 6.20(a).

The dielectric constant exhibits a sharp peak near $T_{N2}$ arising from the onset of ferroelectric ordering in the incommensurate spiral magnetic phase, as explained above section. Above approximately 30 K the dielectric constant for FeVO$_4$ shows a gradual decrease with decreasing temperature, similar to the many insulating materials [209]. Below $\sim$30 K, the dielectric constant increases smoothly with further decrease in temperature, Fig 6.20(b). We attribute this increase in the dielectric constant to the higher order quadratic magnetoelectric coupling $V_4$, rather than spurious electric transport effect, as the resistivity of FeVO$_4$ increases monotonically with decreasing temperature except for a small anomaly at $T_{N2}$, as shown in Fig 6.20(a). Although our magnetic data show that FeVO$_4$ does not order magnetically until cooled to $T_{N1}$, heat capacity measurements suggest the presence of short range spin correlations developing well above this temperature [71]. We propose that these short-range magnetic correlations is the main source for the non-monotonic temperature dependence of the dielectric constant of FeVO$_4$, analogous to the very similar observed effect in other systems such as TeCuO$_3$ [65] and Mn$_3$O$_4$ [210].

Fig 6.20(c) shows plots for the dielectric constant measured at numerous different applied magnetic field. These show a clear shift in the dielectric anomaly towards the lower temperature with increasing applied magnetic field, suggesting strong spin-charge coupling in FeVO$_4$. We observed a reduction of 0.7 K in transition temperature in a magnetic field
Figure 7.11: (a) Temperature dependent dielectric constant and resistivity for FeVO$_4$ bulk ceramic at H=0 T (b) Temperature dependence of dielectric constant near $T_{N1}$ (c) Temperature dependence of the dielectric constant at H=0, 20, 40, 50 and 80 kOe.
H = 8T. The ferroelectric ordering producing this dielectric anomaly is associated with the lower antiferromagnetic transition $T_{N2}$, which will shift to lower temperatures in an applied field.

### 7.2.6 MAGNETODIELECTRIC COUPLING IN BULK FeVO$_4$ CERAMIC SAMPLES

Motivated by this evidence of strong magnetoelectric coupling in FeVO$_4$, we measured the dielectric response of bulk FeVO$_4$ while sweeping the magnetic field at fixed temperatures. These results are shown in Fig 6.21. We plotted the relative change in dielectric constant $\Delta\epsilon(H)/\epsilon(0) = 0$ versus H and a vertical offset was introduced for clarity.

At an intermediate temperature $T=17$ K between $T_{N1}$ and $T_{N2}$, we observe a small negative magnetocapacitance, with the dielectric constant being reduced by 0.03% in field of $H=80$ kOe. As the temperature approaches the multiferroic transition at $T_{N2}$, we noticed
qualitative changes in the magnetocapacitance. By $T=15$ K the magnetocapacitance shift is positive for small fields, with a shift in dielectric constant on the order of 0.02%. The magnetocapacitance response is maximum near $T=14.5$ K, where the dielectric constant being reduced by approximately 0.1% in a field of $H=80$ kOe. At still lower temperatures the magnitude of the magneocapacitance becomes smaller.

Another interesting feature observed in these isothermal magnetocapacitance curves, shown in Fig 6.21, is the presence of clear maxima, which varies as a function of temperature and magnetic field. These maxima appear first at small fields at $T=14.5$ K, then shift to higher fields as the temperature is reduced. These anomalies are different than the dielectric anomaly at $T_{N2}$ and do not reflect the suppression of multiferroic transition temperature in a magnetic field; these dielectric anomalies persist to temperatures 2 K or 3 K below $T_{N2}$, while the maximum suppression of $T_{N2}$ was only 0.7 K at $H=80$ kOe. The dielectric coupling is expected to depend on the symmetry of the magnetically ordered state [8] [65], so a field induced spin reorientation crossover could potentially produce the low temperature dielectric anomaly observed in Fig 6.21. One possibility is that the external magnetic field serves to reduce the slight geometrical frustration in FeVO$_4$ allowing a different spin structure to emerge. Alternatively the spin orientation could be a spin-flop transition as observed in TbMnO$_3$ [211]. We note that FeVO$_4$ remains ferroelectric at high magnetic fields [71], so the modified spin structure would still need to transform as defined by Eq (3) of the reference [89].

### 7.2.7 Magnetodielectric Properties and Electric and Magnetic Field Control of Multiferroic Transition

We studied the dielectric response of FeVO$_4$ thin films to probe the electric field dependence of the multiferroic transition. The trilinear magnetoelectric coupling that produces
the multiferroic functionality in the system is given as

\[ V = 2 \sum_{\gamma} r_{\gamma} |\sigma_1(\vec{q})\sigma_2(\vec{q})| \sin(\phi_2 - \phi_1) P_{\gamma} \]  \hspace{1cm} (7.2)

also results in an electric field (\(\vec{E}\)) dependence of the magnetic structure through the coupling term in the free energy as

\[ \Delta F = -\vec{P} \times \vec{E} \]  \hspace{1cm} (7.3)

To observe the field dependence of multiferroic transition, we first confirmed that FeVO\(_4\) thin films are multiferroic using dielectric and pyrocurrent measurements, as shown in Fig 6.22(a). The clear dielectric anomaly at \(T_{N2} \sim 15\) K substantiate that these FeVO\(_4\)/Si thin films exhibit multiferroic behaviour. The magnitude of the dielectric constant for the FeVO\(_4\) thin film samples was roughly \(\sim 22\), which is slightly higher than that found for the ceramic samples. We attribute this discrepancy mainly to the uncertainty in accurately determining the geometrical factor for these thin films. The dielectric response for these thin film samples is approximately independent of measuring frequency and the loss for this films is \(\tan\delta \sim 0.01\). We attribute this loss mainly to the presence of pinhole defects in the thin film sample, which can be seen in the SEM micrograph in Fig 6.12(a). The zero field temperature dependent dielectric constant, measured at 30 kHz, is shown in Fig 6.22(a).

There is a sharp peak near \(T_{N2} = 15\) K, associated with the development of ferroelectric order in these thin film samples. We note unlike the measurements on bulk sample shown in Fig 6.20(a), the background dielectric constant for FeVO\(_4\) decreases with decreasing temperature. We attribute this to the larger conductivity of the thin film samples arising from the presence of the pinhole defects. We also confirmed that the low temperature phase is ferroelectric by integrating the pyrocurrent after poling at positive and negative fields to yield the spontaneous polarization. These results are shown in the inset of Fig 6.22(a) and
Figure 7.13: (a) Temperature dependent dielectric constant for FeVO$_4$ thin films at H=0 T with inset showing polarization measured at poling fields $E_{pole} = \pm 10$ MV m$^{-1}$. (b) Temperature dependent dielectric constant measured at $E=0$ and $E=3.75$ MV m$^{-1}$ (background was subtracted for clarity).
indicate a spontaneous polarization of $6\mu C m^{-2}$, consistent with our previous measurements on polycrystalline bulk FeVO$_4$. Measurements of the dielectric response for FeVO$_4$ thin film under applied magnetic field yield a suppression of the multiferroic transition temperature very similar to that observed in bulk, as shown in Fig 6.20(c).

To probe further the electric field control of the multiferroic phase transition temperature, we measured the temperature dependent dielectric response in the FeVO$_4$ thin film as a function of bias voltage. Focusing on thin film samples allows the application of relatively large electric fields (on the order of MV/m) with only a relatively small applied bias voltage. We monitored this transition using dielectric measurements because the magnetic anomaly at $T_{N2}$ can not be clearly discerned in these thin film samples. The temperature dependent dielectric constant measured at $E = 0$ and $E = 3.75$ MV/m is shown in Fig 6.22(b). With the application of an electric field, the dielectric peak shifts upward in temperature, by approximately 0.25 K in a field of $E=3.75$ MV/m. We note that any sample heating, which is expected to be negligible in any case because of the low dissipation, would raise the sample temperature relative to the thermometer temperature, leading to a measured decrease in transition temperature. This increase in transition temperature is consistent with an external electric field promoting the development of ferroelectric order and is similar to what has been observed previously in multiferroic Ni$_3$V$_2$O$_8$ films [212]. The relatively small increase of the ferroelectric transition under such large applied electric fields can be directly attributed to the very small polarization in FeVO$_4$ samples. We confirmed that the dielectric anomaly in Fig 6.22 (a) can still be associated with the multiferroic transition, even in the presence of an electric fields, by measuring the response under the simultaneous application of magnetic and electric field.

The magnetoelectric and magnetodielectric studies on bulk and thin film FeVO$_4$ samples are summarized in Fig 6.23. We plot the E-field and H-field dependence of the multiferroic transition temperature in FeVO$_4$ ($T_{N2}$) in Fig 6.23, where CI and NCI represent the collinear
incommensurate and non-collinear incommensurate magnetic structures below $T_{N1}$ and $T_{N2}$ respectively. This transition temperature is monotonically suppressed in an applied magnetic field, decreasing by approximately 0.7 K in an applied field of $H = 80$ kOe. The transition temperature, however, increases systematically with increasing bias voltage, shifting upwards by 0.25 K in an electric field of roughly 4MV/m. The magnetic field dependence of the CI-NCI phase boundary is expected to follow $\Delta T_N \propto H^{1/2}$, while the electric field dependence should be $\Delta T_N \propto E^{1/(\beta+\gamma)}$ respectively [212].

The magnetodielectric coupling in FeVO$_4$ allows us to tentatively identify the onset of short-range magnetic correlations, indicated by the increase in the dielectric constant below T=30 K, as shown in Fig 6.20(b), and also to propose the possibility of a spin reorientation cross-over, based on the field dependent dielectric anomalies in Fig 6.21. We plot the temperature and magnetic field dependence of the proposed spin reorientation cross-over boundary, together with the magnetic field dependence of $T_{N2}$. This is shown in Fig 6.23(right), labeled as NCI*. The two phase boundaries do not coincide so the dielectric anomalies in Fig 6.20(c) are not likely to be associated with the $T_{N1}$ to $T_{N2}$ magnetic transition, but
are tentatively attributed to a field-induced change in magnetic structure. Magnetic field dependent specific heat measurement do not show any additional anomalies at this proposed cross over, suggesting there is a negligible change in entropy between the two spin structures.

### 7.3 CONCLUSION

We have investigated a new multiferroic in the transition metal vanadate family, FeVO$_4$, where only Ni$_3$V$_2$O$_8$ system was previously known to exhibit multiferroic properties. We have synthesized bulk FeVO$_4$ ceramic samples using both organic precursors and an solid state reaction technique and FeVO$_4$ thin films using rf magnetron sputtering. Our magnetic and thermal investigations of FeVO$_4$ exhibit two magnetic transitions at $\sim 22K$ and $\sim 15K$, where ferroelectricity develops at the second magnetic transition $\sim 15K$. We also have observed higher order magnetoelectric coupling well above the multiferroic transition where trilinear magnetoelectric coupling is more pronounced. The magnetic and electric field dependence of the multiferroic transition was investigated using temperature dependent dielectric constant under different applied fields. These studies exhibit the cross control of multiferroic transition using magnetic and electric field and thus confirm the analogous result observed in case of Ni$_3$V$_2$O$_8$, suggesting it is a generic propeties of multiferroics. These studies led to a E-H-T phase diagram for FeVO$_4$ system. We also found evidence for a magnetic field induced spin flop transition in the multiferroic phase.
Chapter 8

CONCLUSIONS

This thesis summarizes my studies on three distinct multifunctional systems, consisting of III-nitride compound semiconductors, which have complementary optical and electrical properties, oxide semiconductors, which exhibit magnetic and electrical responses, and magnetoelectric multiferroics, which are simultaneously magnetic and ferroelectric. These multifunctional systems are expected to play an important role in promoting the development of new multifunctional devices such as charge-spin coupled spintronic devices, high efficiency electro-optic filters, and integrated logic and storage elements.

The emphasis in the III-nitride was to study highly degenerate n-type InN thin films, along with related systems such as In$_{1-x}$Ga$_x$N and In$_{1-x}$Cr$_x$N thin film systems, in order to probe the interplay between the electrical, optical, and magnetic properties. These studies required establishing the parameters to fabricate InN and In$_{1-x}$Cr$_x$N thin films using rf magnetron sputter deposition. One of the principal experimental parameters used to modify the film properties was the oxygen stoichiometry, specifically considering how excess oxygen produces additional charge carriers, modifying the electrical and optical response. Our studies suggest that oxygen incorporates in InN as a donor point defect center to a critical concentration, beyond which oxygen is included as secondary phases such as In$_2$O$_3$ or InN$_x$O$_y$ in the InN host matrix. The oxygen fixed in these impurity phases does not produce
additional charge carriers due to the higher bandgap and insulating properties of the oxide phases. This leads to the observation that highly degenerate n-type InN systems exhibit electronic and optical properties that are independent of oxygen content above some critical oxygen concentration. While such high carrier concentrations are generally unfavorable in semiconducting devices, we have shown that the plasmon frequency on these materials can be tuned from 0.45 eV to 0.8 eV by varying the oxygen content during synthesis. The strong plasmon absorption in the IR regime prompts us to suggest that these highly degenerate InN thin films can be used for applications such as plasmon filters in thermophotovoltaic cell, optical filters and infrared devices. This particular result highlights the types of new properties that can lead novel applications emerging from multifunctional materials.

The work conducted for this thesis has been integral in identifying additional multifunctional properties in degenerate InN films, namely the development of magnetism on introduction a small amount of Cr in these samples. We found that adding 2% and 5% Cr to these InN thin films produces a high n-type carrier concentration $\sim 10^{20} cm^{-3}$, attributed to oxygen defects introduced during fabrication, but also to room temperature ferromagnetic order. These systems were confirmed to have a finite spin polarization of the conduction electrons at low temperature using Point Contact Andreev Reflection, establishing their suitability for some spintronic applications. Although the III-V GaMnAs p-type system, where magneto-transport measurements have confirmed carrier-mediated ferromagnetism, has been studied in depth, the critical temperature for this system falls below $\sim 200K$, making it unsuitable for room temperature applications. Therefore, the multifunctional semiconducting and magnetic properties in Cr:InN make this system particularly attractive for devices.

Another important multifunctional system studied is In$_2$O$_3$, a semiconducting material that can exhibit additional properties by introducing oxygen vacancies or by using other techniques to modify the structure. These additional properties include remarkable optical properties, evidenced by the production and very slow recombination of n-type carriers upon
UV-irradiation and changes in the optical and electronic properties depending on the degree of oxygen off-stoichiometry, and magnetic properties, with room temperature ferromagnetism developing in defect-rich In$_2$O$_3$ samples. On UV irradiation the as-grown In$_2$O$_3$ thin films show a sudden drop in resistivity, due to the excitation of additional electrons. While this photoconductivity is a common feature in many semiconductors, these induced charge carriers in In$_2$O$_3$ have a very long recombination time meaning that quasi-stable control of the electrical transport can be triggered by UV light. Furthermore, since In$_2$O$_3$ is transparent to optical wavelengths, even after vacuum annealing to produce the high conductivity state, this material could be used as a transparent conducting oxide without additional donors being doped into the system. Vacuum annealed In$_2$O$_3$ thin films exhibit good electrical conductivity over a long temperature range with a reasonable mobility of $\sim 40cm^2V^{-1}s^{-1}$, making them suitable for photovoltaic cells, displays, and other applications not requiring fast switching speeds. More interestingly oxygen deficient In$_2$O$_3$ exhibits high temperature ferromagnetism, with the transition temperature well above room temperature. Our high resolution transmission electron microscope (HRTEM) microstructural studies suggest that the high temperature vacuum annealing responsible for promoting the development of ferromagnetic order not only creates oxygen vacancies but also introduces indium vacancies as a result of In-In clustering in the system. This supports recent theoretical predictions that argue that both In vacancies and high carrier concentrations are required to develop ferromagnetism n-type In$_2$O$_3$ system [28].

Additionally I have investigated a number of difference magnetoelectric multiferroic , specifically focusing on the problem of cross-control of magnetic and ferroelectric order parameters by electric and magnetic fields respectively. This work includes studies on the magnetic, dielectric, thermal, and magnetoelectric properties of multiferroic YMnO$_3$, where magnetic and ferroelectric transition temperatures are widely separated, having non-magnetic In substituted for Mn, leading to the YMn$_{1-x}$In$_x$O$_3$ solid solution for $0 < x < 1$. The antifer-
romagnetic ordering transition temperature in the parent compound is suppressed linearly with increasing In atomic fraction, with the reduction consistent with scaling arguments for two dimensional systems. More remarkably, the magnetodielectric coupling associated with multiferroic phase persists in these In substituted samples and we find a strong enhancement in the magnetocapacitive coupling with In substitution. This increase in magnetodielectric coupling on doping with a non-magnetic ion points to the complexity of the mechanism producing the spin-charge coupling in this system.

We have also explored the optical, electronic, and magnetoelectronic properties of two transition metal vanadate oxides, \( \text{Ni}_3\text{V}_2\text{O}_8 \) and the newly identified \( \text{FeVO}_4 \). These materials fall into a different class of multiferroics for which the onset of ferroelectric order coincides with a magnetic ordering transition. This research involved improving the synthesis of both \( \text{Ni}_3\text{V}_2\text{O}_8 \) and \( \text{FeVO}_4 \) in ceramic and thin film geometries, along with studies on the microstructural, optical, electronic, magnetic, ferroelectric and magnetoelectric properties of these systems. The optical and electronic studies suggest that both \( \text{Ni}_3\text{V}_2\text{O}_8 \) and \( \text{FeVO}_4 \) are direct bandgap materials with \( E_g \sim 2.25 \) eV and \( 2.70 \) eV respectively, leading to intriguing possibilities for incorporating these materials in electro-optical applications. The Fermi level of these systems lies approximately equidistant between the conduction and valance band edges, explaining the highly insulating behaviour of these systems. More interestingly we observe very clear \( d - d \) interband transitions in the optical spectra for \( \text{Ni}_3\text{V}_2\text{O}_8 \). These are absent in \( \text{FeVO}_4 \) because Fe is in the high spin electronic configuration in the octahedral crystal field. The magnetoelectric investigations of these system confirm the strong coupling between the magnetic and ferroelectric order parameters. For first time, we demonstrated the direct control of a multiferroic transition temperature using either electric and magnetic fields, or applying both simultaneously, using dielectric spectroscopy for \( \text{Ni}_3\text{V}_2\text{O}_8 \) and \( \text{FeVO}_4 \) thin films. This result is significant because it confirms the generic feature of cross control of the magnetic and ferroelectric order parameters by electric and magnetic fields respectively.
in multiferroic materials, which is crucial for many of the applications proposed for these materials.

The diverse materials discussed in this thesis are unified by the common theme of possessing multiple functionalities. Whether optically active semiconductors, like the degenerate InN based systems, ferromagnetic semiconducting oxides, such as In$_2$O$_3$, or magnetic/ferroelectric systems like FeVO$_4$, all of these materials exhibit complex behavior, indicative of very rich physics, which is, for the most part, still poorly understood. Furthermore, the co-existence of multiple physical responses make these materials intriguing candidates for developing novel devices. For example, a tunnel junction with a multiferroic insulating barrier is expected to exhibit both magnetoresistance (MR) and electroresistance (ER), which could be exploited to produce a fast response, low energy, four state memory system. The ferromagnetic oxide semiconductors considered in this thesis offer the potential to yield a mechanism for injecting spin polarized electrons into silicon at room temperature, which would be an important step in the long development of viable spintronics devices. The tunable plasmon-mediated infrared absorption in degenerate InN films could, potentially, be used to develop new optoelectronic components, which could be crucial for furthering optical computers. The ability to combine and couple multiple distinct materials properties in a single system offers incredible opportunities to design and engineer materials to develop an almost limitless bounty of new devices. Although there remains considerable work to be done before these materials are fully understood, this thesis highlights a number of important consideration, addresses a number of fundamental issues, and provides a platform for future developments in this field.
APPENDIX A

.1 Energy band model

Consider an isolated silicon (Si) atom. The atomic number is 14 leading to a filled shell electronic configuration of 1s$^2$, 2s$^2$2p$^6$,3s$^2$,3p$^2$ or [Ne],3s$^2$,3p$^2$. Of these 14 electrons, 10 electrons are tightly bound to the nucleus and are unlikely to be perturbed by typical atomic interactions. The remaining four electrons are more weakly bound and, in their unperturbed state, will occupy four of the eight allowed energy states (two 3s plus six 3p orbitals) above the filled core. Now consider an array of N isolated, non-interacting Si atoms. There will be a total of 8N available energy states filled by the 4N available electrons. In the absence of interactions, each Si will have identical, discrete electronic energy levels. This is illustrated in Fig 1. As the interatomic distance decreases and atoms come together, the orbitals start overlapping and thus increasing interactions among orbitals shift the energy levels.

This interaction gives rise to a continuous spectrum of allowed electronic energy states, called bands. When the interatomic distance approaches the Si crystal lattice spacing, the distribution of allowed energy states consists of separate bands. In the case of Si, there is a band gap between the filled and unfilled bands, which does not contain any electron states. The filled band at the bottom of the band gap is called the valence band and empty band just above the band gap is called the conduction band. The 4N available electrons will start filling the lowest bands states up through the valence band. As each allowed energy state can have only one electron due to the Pauli exclusion principle, all 4N valence band states
will be filled by these available electrons so the valence bands will be completely filled and conduction band will be completely empty. This is the ideal situation and is true only at absolute zero temperature (0K).

In crystalline materials, the allowed electronic energy states are not the discrete atomic states but consist of allowed energy bands because of interactions. A plot of allowed energy states with respect to some preferred crystal direction is called an energy band diagram, with a representative example shown in Fig 1. A simplified energy band diagram is shown in Fig 2.1, which consists of the highest valence band energy, $E_V$ and the lowest conduction band energy, $E_C$, with an energy difference $E_g$, which is the difference between $E_C$ and $E_V$ ($E_g = E_C - E_V$).
APPENDIX B

Proper materials synthesis is an absolutely crucial component for the development and realization of new functional materials and determining their possible applications. The materials used in the present work include both bulk ceramics and thin films of various multifunctional oxide and nitride systems. The bulk samples were prepared using metal organic solutions and solid state reactions while the thin films were prepared using radio frequency (RF) magnetron sputtering system and spin coating with metalorganic decomposition (MOD). These methods of sample preparation are described below.

.1 Synthesis of Bulk Material

There are numerous techniques for synthesizing bulk ceramic materials such as mechanical methods, which includes solid-state reactions, ball milling and chemical methods, which includes sol-gel and metal organic solutions. Each technique has certain benefits and drawbacks. We have used solid state reaction techniques for the preparation of ceramic Ni$_3$V$_2$O$_8$ and FeVO$_4$ samples, and metal organic solution technique for FeVO$_4$ samples.

.1.1 Solid State Reaction Technique

Solid state reaction (SSR) technique is an easy and convenient technique for the preparation of bulk ceramic samples, particularly oxides. The main steps involved in the process are summarized in Fig. 2. Starting from binary oxides, for example nickel oxide (NiO) and
vanadium oxide ($V_2O_5$) for preparing $Ni_3V_2O_8$ and iron oxide ($Fe_3O_4$) and vanadium oxide ($V_2O_5$) for preparing $FeVO_4$, are measured so the metal ions are in the desired stoichiometric ratio then mixed homogeneously using a mortar and pestle, followed by wet mixing in ethanol to ensure better homogeneity. This solid solution was heat treated at 600°C for both $Ni_3V_2O_8$ and $FeVO_4$ systems for 4 hours in air and re-ground. This process of intermediate grinding followed by thermal annealing in air was repeated several times to complete the solid state reaction and ensure a fully reacted and uniform composition. The homogeneous solid solution was finally calcinated in air at 1000 °C and 800 °C for 4 hours for $Ni_3V_2O_8$ and $FeVO_4$ respectively, to obtain stoichiometric single phase materials.

These stoichiometric $Ni_3V_2O_8$ and $FeVO_4$ powders were also used to prepare the sputtering targets to fabricate the thin film samples. Approximately 30 g of powder for each system was mixed with 15 mL of 2 mole percent polyvinyl alcohol (PVA) as a binder. The dried powders were pressed into a circular discs having a diameter of approximately 50 mm with
a thickness of 2.5 mm by using 2” inch die and hydraulic pressure on the order of 2000 psi. These discs were annealed in air at 600°C for 4 hours to burn off the residual organics. A final thermal annealing in air at 1000°C and 800°C for 4 hours was performed to produce dense pellets of Ni$_3$V$_2$O$_8$ and FeVO$_4$ respectively, used for the sputtering targets.

### 1.2 Metal Organic (MO) Solution Deposition

This process of making ceramic samples is similar to the solid state reaction technique except the starting materials are metal organic solutions in contrast to the binary oxides powders for SSR. A homogeneous mixture of constituent metal organic solutions in appropriate stoichiometric ratio is prepared. For example a homogeneous mixture of iron (II)-2 ethylhexanoate and vanadium naphthenate organic solutions having Fe to V atomic ration 1:1 would be used for synthesis FeVO$_4$. The well-mixed solution was heated slowly to 350°C for 2 hours to burn off the organic constituents in the solution. The resulting powder is calcinated at 800°C for 2 hours in case of FeVO$_4$ system, resulting in a stoichiometric single phase material. A very similar process can be employed for other ceramic samples to obtain single phase materials having the correct stoichiometry. One important advantage of the MO solution process is that the higher degree of homogeneity in the precursor mixture leads to more homogeneous samples. This technique is therefore suitable for making small amounts of sample.

### 2 Thin Film Synthesis

There are a number of techniques for preparing thin film samples, including metal organic decomposition (MOD), metalorganic chemical vapour deposition (MO-CVD), pulsed laser deposition (PLD), sputtering, molecular beam epitaxy (MBE), among others. Each technique has a number of advantages and disadvantages. The thin films used for this study
have been prepared mainly using radio frequency (RF) magnetron sputtering.

2.1 RF Magnetron Sputtering Deposition

Sputtering is a thin film deposition process where the sputtered or eroded atoms from a target deposit onto the substrate. This process is not in thermodynamic equilibrium as the ejected sputtered atoms into the gas phase are not in equilibrium. This allows the deposition of a wide variety of films, such as: metallic, semiconductors, and highly insulating oxide systems such as ferroelectric and multiferroic systems. The sputtering process involves momentum exchange between the background ions in the chamber and the constituents of the target material. The incident ions initiate collision cascades in the target. When these cascades recoil and reach the target surface at an energy above the surface binding energy, an atom can be ejected. The average number of atoms ejected from the target per incident ion is called the sputtered yield and depends on a number of factors including ion incident angle, ion energy, mass of ions, target system and the surface binding energy of atoms in the target. There are different types of sputtering techniques, DC (diode) sputtering, RF (radio frequency) sputtering, and magnetron sputtering, which is generally, used in combination with either DC or RF sputtering. The target is connected to a large negative bias in DC sputtering or a large RF bias in RF sputtering. For magnetron sputtering, strong magnets in a circular geometry are mounted below the target. The field from these magnets traps free electrons just above the target surface, which are therefore not able to hit the substrate, which is a problem in DC sputtering. In addition, these electrons, localized near the target by magnetic field, significantly enhances probability of ionizing the background gas molecules. This increase in the ionic density substantially increases the rate at which the target material is eroded and the deposition rate onto the substrate. The ejected target atoms are neutrally charged and thus are not affected by the magnetic field. Magnetron sputtering produces a high deposition rate and avoids problems with substrate heating and structural damage by
electron bombardment, both of which negatively impact DC sputtering.

We used reactive RF magnetron sputtering to prepare binary nitride and oxide semiconducting films and numerous ternary oxide multiferroic thin films. These thin films were deposited on (0001) c-axis sapphire and (100) conducting Si substrates. These substrates were cleaned in acetone followed by methanol and deionized water. The dried cleaned substrates were mounted onto the substrate holder. The sputtering chamber was evacuated to high vacuum ($\leq 10^{-6}$ Torr) and left for $\sim$12 hours to remove any residual gaseous impurities. A mixture of high purity Argon (partial pressure $\sim 1.35 \times 10^{-2}$ Torr) as the sputtering gas and oxygen or nitrogen (partial pressure $\sim 1.50 \times 10^{-3}$ Torr), as the reactive gas were introduced into the chamber. Different substrate temperatures were used for different systems. The quality of the films depends on numerous parameters such as applied power, substrate temperature, distance between target and substrates, the ratio of sputtering and reactive gases ratio. It was therefore necessary to carefully adjust these parameters to optimize the sample properties. This RF magnetron sputtering technique offers numerous advantages over other thin film growth techniques such as a high deposition rate, better thickness uniformity, relatively better structural quality. However, this process is not very appropriate for the layer by layer growth of thin films, which is important in depositing epitaxial quality thin films, and is generally achieved using pulsed laser deposition (PLD) or molecular beam epitaxy (MBE).
APPENDIX C

After synthesizing bulk ceramic samples or fabricating thin films, we need to characterize the material properties to improve these properties during post processing as well as probe the physics underlying the behavior. We used a number of different techniques to explore the structural, optical, electronic, magnetic and magnetoelectric properties of these materials. A brief introduction to the techniques used in this study is given below.

.1 Structural And Microstructural Characterization

The structural and microstructural properties of these materials were investigated using powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and are described below.

.1.1 X-Ray Diffraction (XRD)

The X-ray diffraction can be used to investigate the phase formation, crystal structure, lattice parameter and presence of secondary phases for both bulk ceramic and thin films system. The wavelength of the X-rays is comparable to interatomic spacing, making this a suitable technique to probe the structural arrangements of atoms inside the crystal lattice. A Rigaku RU2000 X-ray powder diffraction system, with Cu Kα radiation (1.54178 Å) was used to investigate the crystal structure of bulk and thin film systems used for this study. The monochromatic and collimated X-ray beams are incident on the sample at an angle θ
to the plane of sample and are diffracted by the crystal planes according to Bragg’s law

\[ 2d_{hkl} \sin(\theta_{hkl}) = n\lambda \]  

where \( d_{hkl} \) is the spacing between the hkl planes, \( \lambda \) is the incident X-ray wavelength, in this case 1.54178 Å, and \( n \) is order of diffraction. A schematic for a typical X-ray diffraction experiment is shown in Fig [NUMBER]. The intensity of the diffracted X-rays is measured as a function of the diffraction angle \( 2\theta \) and the sample orientation \( \theta \) with respect to the incident beam, leading to the \( \theta - 2\theta \) XRD pattern. This \( \theta - 2\theta \) diffraction pattern is used to identify the crystalline phase and the crystal structure of the sample. The size of small crystalline regions i.e. grains can be calculated using Debye-Cheerrr’s formula [PUT IN REFERENCES][B. D. Cullity and S. R. Stock, Elements of X-Ray Diffraction, 3rd Ed. Prentice-Hall Inc., (2001)]

\[ \tau = \frac{K\lambda}{\beta \cos(\theta)} \]  

where \( K \) is the shape factor and is close to unity (\(~0.9\) ), \( \lambda \) is the X-ray wavelength ( 1.54178 Å), \( \beta \) is the diffraction peak broadening at half the maximum intensity (FWHM = Full Width at Half Maximum) in radians and \( \theta \) is corresponding Bragg angle.

### 1.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is an important material characterization tool used to visualize and investigate the surface morphology and related features. In an SEM system, an electron gun (either a thermionic electron gun such as tungsten or lanthanum hexaborate LaB\(_6\) or a field emission electron gun) generates a beam of high energy electrons, which passes through a series of magnetic lenses (condenser and objective lenses), which can be used to focus the electron beam on the surface of sample. When this focused electron beam strikes and interacts with the sample surface, it creates various electron signals,
such as secondary electrons, backscattered electrons, together with radiation signals, including visible radiation and characteristic X-ray photon radiation from the interaction volume underneath the sample surface.

In general, the interactions between the high energy electron beam and sample surface are divided into two categories: elastic interactions, where the electron beam strikes the sample, and the electrons reverse their direction without changing energy producing backscattered electrons and inelastic interactions, where incident electrons collide with an orbital electron in the sample, causing (1) the ejection of new electrons, known as secondary electrons and (2) the emission of visible or characteristic X-ray radiation. Secondary electrons usually come from a region close to the surface, which provides information on the surface morphology. Backscattered electrons and X-ray radiation are produced in deeper region of the interaction volume and provide information about the chemical distribution of the sample. We have used a Hitachi S-2400 SEM to characterize both the ceramic and thin films samples used in
this study, in order to study the surface morphology, surface defects for thin film samples, and crystallite size and morphology for bulk samples. We also carried out cross-sectional SEM studies on thin film samples to examine their thickness, substrate-thin film interface quality, and the distribution of defects across the film. The associated energy dispersive spectroscopy (EDS) X-ray detector accessory was used to analyze the chemical distribution of elements in the sample.

1.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a versatile imaging technique used to probe nanoscale structure. This is an analog to the optical microscope where high energy electrons are used as an incident beam like light waves in optical microscope. The resolving power 'd' (or minimum resolvable separation between two object points) of an optical microscope is given by

\[ d = \frac{0.612 \lambda}{n \sin \alpha} \]  

where \( \lambda \) is the wavelength of the light source, \( n \) is the refractive index of the medium between the specimen and the objective lens and \( \alpha \) is the half angle in radians of the cone of light from the sample plane to the objective. The product \((n \sin \alpha)\) is known as the numerical aperture (NA) of the objective lens. This leads to resolving powers of the typical optical microscopes on the order of \(\sim 0.2 \mu m\) due to the the diffraction limit of the visible light with wavelength range 400 nm to 700 nm. Thus sample features beyond this limit, such as the distribution of atoms in the crystal lattice, defects such as void, interestials and inclusions are not detectable using optical microscopy. The wavelength of electrons in TEM can be made very short by increasing the accelerating voltage to several hundred kilovolts, which produces a resolution of \(\sim 0.05 \text{ nm} \). This high resolution possible in a TEM, makes it an important structural and microstructural characterization tool to visualize the crystal
lattice, defects such as interestials, planar defects. We used a JOEL-2010 TEM operating at 200 KV to investigate the samples used in this study. Samples for cross-sectional TEM were prepared by a mechanical process. The samples were attached (with glue) to a smooth surface followed by mechanical thinning to few micrometers. Finally, the samples were ion milled to a final thickness \( \leq 200 \) nm. The thinned samples were mounted on a TEM grid consisting of Cu metal frame with a carbon based support film. Additionally, we imaged sample flakes scraped from the thin film samples in a separate HR-TEM study to avoid any possible modification of surface introduced during mechanical and ion beam milling.

In transmission electron microscopy imaging, an intense, focused, monoenergetic beam of electrons impinges on the sample. The electron beam is of sufficient energy to, in large part, propagate through the sample. This transmitted beam consists of unscattered central and scattered non-central electrons. The transmitted unscattered electrons form an image, called the bright field (BF) image, while the images generated by scattered non-central electrons are called dark field (DF) images. These two complementary images provide detailed information on the crystal lattice, and microstructural and other related information. TEM can also be used to get diffraction information using the Selected Area Electron Diffraction (SAED) option. This provides additional information on the crystal lattice symmetry and crystal orientation. In addition, elemental analysis of the samples can be carried out using the associated energy dispersive X-ray (EDX) spectroscopy accessory.

1.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique used to probe the elemental composition, chemical stoichiometry, and electronic state of the elements present in the system. In XPS, a monoenergetic soft X-ray beam is bombarded onto the sample under investigation, which penetrate into the material and knock out inner core-level electrons. These electrons are called X-ray photoelectrons. The kinetic energy \( (E_K) \) of these electrons
is related to the binding energy \((E_B)\) (the energy required to remove electron from its initial level to the vacuum level) of the electrons as

\[
E_K = h\nu - E_B
\]

where \(h\nu\) is the energy of the incident X-ray photon. This binding energy \(E_B\) is an intrinsic property and is unique for a given orbital in each element, while the kinetic energy \(E_K\) is not uniquely defined as it varies with the incident photon energy. Thus, knowing the binding energy of the electrons, the chemical elements and their valence states in the constituent system can be determined. The relative concentration of elements can be determined from the measured photoelectron intensities or by integrating the area under the binding energy peaks. This technique is highly surface sensitive; XPS can probe 2-20 atomic layers, depending on the material, incident X-ray photon energy and the angle with respect to the surface of the measurement. We used a Perkin Elmer XPS system for the elemental, chemical and valence state analysis of systems used in this study.

.2 Optical Characterization

.2.1 Raman Spectroscopy

Raman spectroscopy is an important tool for characterizing material properties by probing inelastic scattering signal from the system material under investigation. A monochromatic light source is used in combination with an optical microscope, grating, and CCD detector to measure the Raman signal. The Raman spectrum is the measurement of the inelastic light scattering intensity as a function of wavenumber \(\nu\). This Raman shift in \(\text{cm}^{-1}\). Raman shift is the measure of change in wavenumber (or energy) of the scattered photons
with respect to the incident photon and is given as

$$\tilde{\nu} = \frac{1}{\lambda_{in}} - \frac{1}{\lambda_{sc}}$$  (5)

where $\lambda_{in}, \lambda_{sc}$ are the wavelengths of the incident and scattered light respectively. Raman scattering is an inelastic scattering process, where the incident light beam interacts with the lattice vibrations and the inelastically scattered light either gains or loses energy depending on the interaction process. If the energy of the scattered photon is smaller than that of incident photons, the interaction is known as a Stokes process, while if the scattered photon energy is greater than that of incident photons, the interaction is known as an Anti-Stokes process. This technique is used to probe lattice properties, such as crystal structure, phonon spectrum and lattice dynamics including as phase transitions. Another important application is the identification of defects and impurities present in the system, which are not easily identified using other techniques such as XRD or SEM.

We have used Horiba Triax and Renishaw $\mu$-Raman systems to investigate the room temperature vibrational spectrum of various nitride, oxide and multiferroic systems. An argon-ion green laser with a 514.5 nm (2.41 eV) excitation was used in the backscattering geometry for most these studies. In addition, an optical cryostat was used to conduct temperature dependent Raman spectroscopy for multiferroic systems.

## 2.2 UV-Vis-NIR Spectroscopy

Measurements of the optical bandgap, transmittivity, and reflectivity of materials can provide deep insight into the electronic and optical properties. For example, most of semiconductors exhibit a broad and absorption edge with an attenuation coefficient on the order of $\sim 10^4 cm^{-1}$ or higher from the near-infrared or visible through to the ultraviolet. This absorption arises as photons are absorbed by electrons in the valence band and excited to the conduction band, causing a strong optical absorption near the bandgap energy. This is
known as the optical absorption or electronic bandgap edge of the material and the energy scale is an important characteristic of the system. We have used a Perkin Elmer Lambda 900 UV-Vis-NIR spectrometer to investigate the optical properties of the samples used in this study. This system consists of a UV-Vis-NIR source, a diffraction grating unit, a beam splitter, and two detectors. The incident beam is separated into its component wavelengths by the diffraction grating and divided into two beams of equal intensity, which provide the reference and signal respectively. The intensity of the transmitted beam as a function of wavelength is recorded by detectors. We collected optical transmittance and reflectance spectrum under normal incidence configuration in the range from 175 to 3300 nm, covering the UV-Vis-NIR electromagnetic spectrum. The transmittance and reflectance spectra exhibit well defined interference fringes because of the multiple reflections at the interface of thin film and substrate. These fringes can be used to determine the thickness of thin films as

\[
t = \frac{\lambda_1 \lambda_2}{2(n_2 \lambda_1 - n_1 \lambda_2)}
\] (6)

where \( t \) is the thickness of the film, \( \lambda_1 \) and \( \lambda_2 \) are the wavelengths at two consecutive maxima or minima and \( n_1 \) and \( n_2 \) are refractive indexes at respective wavelengths.

Additionally, we have used the measured optical transmittance and reflectance to determine the absorbance and hence the absorption coefficient as:

\[
\alpha = \frac{-\ln(T(\lambda) + R(\lambda))}{t}
\] (7)

where \( T(\lambda) \) and \( R(\lambda) \) are the relative transmittance and reflectance at a given wavelength \( \lambda \) and \( t \) is the thickness of the film.

The measured absorption coefficient can be used to estimate the electronic bandgap. Furthermore, the transmittance and reflectance spectra can be used to investigate a number of physical and electronic properties such as interband/intraband transitions, high energy
critical points, and plasmon absorption in highly degenerate systems.

.3 Electrical Characterization

Electrical transport properties such as carrier density, sheet and bulk resistivity, and mobility of charge carriers for the nitride and oxide samples were studied using Hall effect measurements. When an electric current passes through a sample in a magnetic field, a potential proportional to the current and magnetic field is generated across the material in a direction perpendicular to both the current and magnetic field direction. This phenomenon is called the Hall effect and the voltage produced perpendicular to both the current and magnetic field direction is called the Hall voltage. The sign of Hall voltage provides the information regarding the type of carriers, whether electrons or holes, and is given by

\[ V_H = \frac{1}{nq} \frac{I_x B_z}{t} \quad (8) \]

where \( n \) is number of carriers per unit volume, \( q \) is the carrier charge with sign, \( I \) is the current across the sample flowing along \( x \) direction, \( B \) is the magnetic field applied along \( z \) direction and \( t \) is the thickness of the sample.

By measuring \( V_H \), one can calculate the effective carrier density in the sample. The quantity \( \frac{1}{nq} \) is called the Hall coefficient, \( R_H \). The Hall voltage \( V_H \), or Hall coefficient \( R_H \), will be negative if charge carriers are electrons and positive if charge carriers are holes.

If the system consists of both electrons and holes as charge carriers, then the Hall coefficient is given as :

\[ R_H = \frac{p \mu_h^2 - n \mu_e^2}{q(p \mu_h + n \mu_e)^2} \quad (9) \]

where \( \mu_h \) and \( \mu_e \) are hole and electron mobilities respectively.
In addition, the van der Pauw technique was used to determine the sheet resistance and bulk resistivity, charge carrier density and their mobility. The advantage of this method is to average out the geometrical effects and thus an arbitrary sample geometry can be used for measurements [213, 214].

.4 Magnetic Characterization

The DC magnetic measurements used in this study were carried out using a Quantum Design Magnetic Property Measurement System (MPMS-5S) SQUID (Superconducting QUantum Interference Device) magnetometer. This system provides a temperature range of 2 K to 400 K with a ±5 T magnetic field variation for different magnetic measurements. The SQUID magnetometer consists of a superconducting magnet to apply the measuring field, a superconducting pick-up/detection coil, a SQUID, and a superconducting magnetic shield [215]. The superconducting detection coil picks up magnetic signal from sample, which is connected to the SQUID device. This device converts a magnetic flux signal to the voltage. For these measurements, approximately ∼5 mg to 80 mg of sample was placed gelatin capsule, followed by clean cotton, to avoid any movement of the sample. This gel capsule was then mounted in a drinking straw where this capsule was fixed by sewing it at a fixed distance, to avoid any movement of this capsule during magnetic measurements. This straw was finally attached to the MPMS sample probe. The details of sample preparation for magnetic measurements are given in reference [216]. When this sample moves up and down, it produces an alternating magnetic flux in the detection coil. This magnetic flux is converted into an alternating output voltage in SQUID device, which is amplified and measured by the system electronics. This output voltage, which is proportional to the sample magnetic moment, is converted into the magnetic moment by the system electronics and software. The temperature dependent magnetic measurements were carried out either on first cooling in the absence of magnetic field and then applied a very small field to measure the magnetic
moments during warming, called Zero-Field Cooled (ZFC) measurements or cooled in the presence of small magnetic field and then followed by magnetic measurement during warming in the same field, called Field Cooled (FC) measurements. In addition, we have also studied the magnetic moment versus magnetic field effect (M-H) at constant temperatures.

In addition to the DC magnetic studies, we also have conducted AC magnetic dynamics using the Quantum Design Physical Property measurement System (PPMS), which offers a temperature range of 2 K - 400 K with a ±9 T magnetic field variation. We typically used measuring frequencies between 100 Hz and 10 kHz for these AC measurements. This system has also an option for the DC magnetic measurements with a smaller detection limit $\sim 2.5 \times 10^{-5}$ emu with respect to Quantum Design MPMS system where detection limit is $\sim 2.0 \times 10^{-8}$ emu. However, PPMS system offers good detection limit $\sim 10^{-8}$ emu for AC magnetic measurements.

.5 Dielectric Characterization

We also used dielectric spectroscopy to study the electronic properties of some of the materials included in this study. These measurements were done using an Agilent 4284A LCR meter for frequencies between 20 Hz and 1 MHz together with temperature and magnetic field control provided by the Quantum Design PPMS. The temperature and field dependent dielectric measurements on bulk powder samples were done in a parallel plate geometry. We cold pressed the samples into a circular pellet of diameter $\sim$4 mm and having a thickness of 1-2 mm. Silver epoxy was used for top and bottom electrodes in conjunction with conducting Cu wires for further connections. The details of dielectric sample preparation and its measurement is given in reference [216]. For thin films samples we used conducting Si (n-type) as a bottom electrode and a small circular Au electrode of $\sim$1 mm diameter and $\sim$50-100 nm thickness, was sputtered at room temperature.

The majority of the temperature dependent dielectric measurements were conducted at
30 kHz excitation frequency and at a moderate warming rate, as these were found to typically provide the cleanest data. The measured capacitance in a parallel plate geometry is directly proportional to the dielectric constant of the material and is defined as

\[ C = \frac{\varepsilon_0 \varepsilon A}{d} \]  

where \( \varepsilon_0 \) is the permittivity of free space i.e. vacuum and is \( 8.85 \times 10^{-12} \text{ F/m} \), \( \varepsilon \) is the dielectric constant, \( A \) is the electrode area of the capacitor and \( d \) is the thickness of capacitor.

## 6 Pyrocurrent Measurement

The pyroelectric current is the current produced by a change in temperature. In order to align the different domains in the ferroelectric materials investigated in this study, the sample were poled by applying an external voltage, known as poling voltage, at high temperatures and cooled through the Curie temperature. The voltage was set to zero before beginning the current measurements. Such cooling under an external poling voltage will align the individual domains. On warming through the phase transition, the spontaneous polarization vanishes, leading to a large change in the electric dipole moment of the sample. This charge can be detected as the current, which is proportional to the rate of change of temperature as

\[ I = p(T) A \frac{\partial T}{\partial t} \]  

where \( I \) is the current, \( A \) is the electrode area, \( \frac{\partial T}{\partial t} \) is the rate of change of temperature with respect to time and \( p(T) \) is the pyroelectric coefficient temperature at temperature. The pyroelectric coefficient is also defined as the rate of change of the spontaneous polarization vector with respect to temperature as

\[ p(T) = \frac{\partial P_s}{\partial T} \]
where $P_S$ is the spontaneous polarization. Upon integrating this equation and substituting for $p(T)$, we get

$$P_S = \int \frac{I}{A} \, dt$$

(13)

This equation shows that by integrating the current density ($I/A$) with respect to time, we can determine the spontaneous polarization.

We used a Keithley 6517 electrometer to measure the pyroelectric current in conjunction with a Quantum Design PPMS to control the temperature and magnetic field. The samples were prepared in a parallel plate capacitor geometry, similar to that used for dielectric measurement. We poled the sample at $\sim \pm 200$ V for bulk systems and $\sim \pm 2$ V for thin film systems, from a temperature above the transition at which it becomes pyroelectric or polar and cooled to low temperature. The electric field was then removed and the top and bottom electrodes were shorted for 2 minutes in order to remove any possible surface charge built up during the poling process. The sample heating rate was kept constant at 4 K/min for most of the samples. The spontaneous polarization was obtained by integrating the pyroelectric current with respect to time. The spontaneous polarization vanishes above the Curie temperature.

.7 Heat Capacity Measurements

We used the standard option on the Quantum Design PPMS for heat capacity measurements for most of the samples used in this study. For the ceramic samples, we mixed approximately $\sim 50$ mg of the sample powder with the same mass of fine silver (Ag) powder thoroughly to insure homogeneity. This homogeneous mixed composite was pressed into small disks to ensure good thermal contact throughout the entire sample. A small amount of thermally conducting N-grease was used to mount the sample on heat capacity puck. The
details of sample preparation and its mounting procedure is given in reference [216] and Quantum Design PPMS Model 6000 Hardware and Options manual.
Bibliography


[213] L. J. van der Pauw, Philips Research Reports, 13, 1(1958)


ABSTRACT

ELECTRO-OPTIC AND MAGNETO-DIELECTRIC PROPERTIES OF MULTIFUNCTIONAL NITRIDE AND OXIDE MATERIALS

by

AMBESH DIXIT

December 2010

Advisor: Dr. Gavin Lawes
Co-advisor: Dr. Ratna Naik
Major: Physics
Degree: Doctor of Philosophy

Materials that simultaneously exhibit different physical properties provide a rich area of research leading to the development of new devices. For example, materials having a strong coupling between charge and spin degrees of freedom are essential to realizing a new class of devices referred to generally as spintronics. However, these multifunctional systems pose new scientific challenges in understanding the origin and mechanisms for cross-control of different functionalities. The core of this Ph.D. dissertation deals with multifunctional nitride and oxide compound semiconductors as well as multiferroic magnetic oxide systems by investigating structural, optical, electrical, magnetic, magnetodielectric and magnetoelectric properties.

Thin films of InN nitride compound semiconductors and closely related alloys have been investigated to understand the effects of intrinsic defects on the materials properties while considering possible applications of highly degenerate InN thin films. As grown rf sputtered
InN films on c-axis (0001) sapphire exhibit highly degenerate n-type behaviour due to oxygen defects introduced during growth. The effect of oxygen in InN matrix has been further investigated by intentionally adding oxygen into the films. These studies confirm that oxygen is one of the main sources of donor electrons in degenerate InN. Above some critical concentration of oxygen, secondary phases of In$_2$O$_3$ and In-O-N complexes were formed. It was also possible to tune the carrier concentration to produce changes in the plasmon frequency, which varied from 0.45 eV to 0.8 eV. This characteristic energy scale suggests that these highly degenerate InN thin films could be used for thermophotovoltaic cells, optical filters, and other IR electro-optic applications.

To probe the magnetism in transition metal doped InN system, In$_{0.98}$Cr$_{0.02}$N and In$_{0.95}$Cr$_{0.05}$N thin films were fabricated. Our results suggest that these films develop ferromagnetic order above room temperature with a spin polarization of $\sim 40\% \pm 5\%$, suggesting strong correlation between electron carriers and observed ferromagnetism.

Another In-based multifunctional material that has been explored is defect-rich In$_2$O$_3$. This system exhibits numerous interesting properties such as being simultaneously transparent and electrically conducting and above room temperature ferromagnetism together with semiconducting properties. The oxygen stoichiometry in In$_2$O$_3$ plays a crucial role in determining its optical, electronic, and magnetic properties. The effect of oxygen vacancies on different physical properties has been investigated. Our results suggest that as grown, nearly stoichiometric In$_2$O$_3$ thin films exhibit strong photopersistent current with very long carrier lifetime. Heat treatment under reduced oxygen environment creates oxygen vacancies in these films, producing electron donors. Thus vacuum annealed In$_2$O$_3$ becomes a highly degenerate n-type conductor. Oxygen deficient In$_2$O$_3$ can be used as transparent conducting oxide without any further doping, which allows the conductivity to be switched reversibly by thermal annealing in air or vacuum. In addition highly oxygen deficient In$_2$O$_3$ films exhibit ferromagnetism above room temperature.
We have also investigated oxide based magnetoelectric multiferroics which show simultaneous magnetic and ferroelectric properties. This study included detailed investigations of YMnO$_3$, Ni$_3$V$_2$O$_8$ and FeVO$_4$, where we have investigated FeVO$_4$ a new multiferroic system in the vanadate family. The main focus of this project was to understand the microscopic origin of the magnetoelectric coupling and cross-control of different ferroic order parameters in these system. We have synthesized bulk Ni$_3$V$_2$O$_8$ and FeVO$_4$ ceramics and characterized the thermal, magnetic, dielectric and magnetodielectric response of these samples in bulk form. To understand the cross-control of magnetic and ferroelectric order parameter we deposited thin films of Ni$_3$V$_2$O$_8$ and FeVO$_4$ systems and investigated their multiferroic properties using dielectric spectroscopy. We have demonstrated the direct control of multiferroic transition temperature with the applied external electric and magnetic fields. These investigations confirm the strong magnetoelectric coupling between different ferroic order parameters in such multifunctional multiferroic systems.
NAME: AMBESH DIXIT

EDUCATION:

Ph. D. (Physics): Wayne State University, Detroit, MI, October 2010.

M. S. (Physics): Wayne State University, Detroit, MI, 2008.

M. Sc. (Physics, Electronics Special): Allahabad University, India

B. Sc. (Mathematics and Physics): Allahabad University, India

SELECTED PUBLICATIONS: