

University of Wollongong
Research Online

University of Wollongong Thesis Collection
1954-2016

University of Wollongong Thesis Collections

2006

Studies on diluted oxide magnetic semiconductors for spin electronic applications

Germanas Peleckis
University of Wollongong, peleckis@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/theses>

University of Wollongong

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Peleckis, Germanas, Studies on diluted oxide magnetic semiconductors for spin electronic applications, PhD thesis, Institute for Superconducting and Electronic Materials, University of Wollongong, 2006.
<http://ro.uow.edu.au/theses/662>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Studies on diluted oxide magnetic semiconductors for spin electronic applications

A thesis submitted in fulfilment of the requirements
for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

GERMANAS PELECKIS, BSc, MSc

Institute for Superconducting and Electronic Materials
and
Faculty of Engineering

2006

DECLARATION

I, Germanas Peleckis, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, in the Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.



Germanas Peleckis

Wollongong

July 2006

Acknowledgements

I would like to thank my supervisors Assoc. Prof. X. L. Wang and Prof. S. X. Dou for giving me the opportunity to work in Institute for Superconducting and Electronic Materials. There are not enough words to express my gratitude for their willingness to share their knowledge with me, numerous discussions and support that they have given me.

My warmest thanks go to Prof. R. S. Liu from National Taiwan University for giving a part of his valuable time to perform XANES measurements, which results were very valuable in this study. I would like to thank Prof. P. Munroe from University of New South Wales for making TEM observations of our samples and valuable discussions.

I also express my gratitude to D. Wexler, R. Kinnel, G. Tilman, N. Mackey and other technical staff of the Faculty of Engineering and our institute for their technical support and assistance in experimental work, various trainings provided for the better understanding of the equipment I used during the course of my PhD studies.

I wish to say big thank-you to Drs. Aleksey Pan and J. Horvat for helping me with magnetic and transport measurements and great care over the measurement equipment. Also thanks to Dr. K. Konstantinov for guidance and training to obtain SEM images of highest quality. I also acknowledge help of Tania Silver in ISEM for correcting my English language in the articles I have submitted to various journals and this thesis itself.

In also want to thank my friends, colleagues at ISEM and especially Scott Needham for being my closest friend and helping me to overcome all the struggles I had during my studies. Many thanks to Dr. G. Alvarez for fruitful scientific discussions and chats about everyday life.

Finally, I want to thank my parents and my wife for being there for me. Without their love, understanding and encouragement this work would be close to impossible to finish.

ABSTRACT

Conventional semiconductor electronics is based on the charge of the electron. For a long time the spin of the electron has been ignored in the field of conventional electronics. Spintronics, also called spin electronics, magnetoelectronics or magnetotronics, is a newly emerging field in solid state physics and information technology. One of the major challenges for semiconductor spintronic devices is to develop suitable novel spin-polarized magnetic semiconducting materials that will effectively allow spin-polarized carriers to be injected, transported, and manipulated. Therefore, searching for new materials has become crucial from the viewpoints of both fundamental research and practical applications.

Diluted magnetic semiconductors (DMS) are one of the most promising candidates for spintronic application. The research on the DMS materials which has been carried out worldwide in the past decade has been reviewed in this thesis. A DMS material can be realized when a conventional host semiconductor, such as GaAs, ZnO, etc., is doped with magnetic impurities, usually transition metal (TM) ions. For practical application, DMS material should favorably be ferromagnetic (FM) at room temperature. Early studies on DMS materials showed that FM can be induced in Mn doped III-V semiconductors. However, these materials are not suitable for practical applications as their Curie temperatures are quite low. On the other hand, some theoretical works predicted room temperature ferromagnetism in TM doped oxide semiconductors. This fact has boosted research in the field of DMS materials. The number of reports on observations of room temperature FM in Co, Mn, Ni, and Cr doped ZnO and TiO₂ semiconducting oxides is constantly growing.

The aim of this thesis was to study the doping effects of transition metal ions on the structure, transport, and diluted magnetic properties of various host oxide semiconductors. The oxide semiconductors investigated in this work are: ZnO, CuO, Ga₂O₃, and In₂O₃. A search for room temperature ferromagnetic semiconductors was the key point of this research. In addition, we have tried to understand and explain the

possible origins of the magnetic properties of the samples produced, because at the present time there is no firm theoretical model that could explain magnetism in DMS materials.

The majority of the samples studied in this research were prepared by a conventional solid state synthesis technique. We have carried out X-ray diffraction and electrical-magnetic transport measurements to determine the crystal structure, electrical and magnetic properties of our samples. In order to investigate the valence state of transition metal ions in the prepared materials, X-ray absorption near edge spectroscopy analysis was used.

The major results from this PhD study are:

(1) Polycrystalline Co-doped ZnO oxide samples were prepared with Co doping levels varying between 1 and 10%. All samples were found to be paramagnetic without any trace of ferromagnetism at room temperature and were insulators. Introduction of In ions into the system decreased the electrical resistivity of the samples. The spin state assessment revealed that strong spin-orbital coupling is present in In containing samples. Valence state assessment showed that in ZnO Co is present in the 2+ valence state.

(2) Mn doped CuO bulk samples showed a ferromagnetic transition at 80 K. All the samples prepared were insulating. In and Zn were used as charge donors. It was found that the In solubility limit in CuO lattice is very limited, less than 1%. The magnetic properties that were measured showed a large decrease in the magnetic susceptibility of (Mn,Zn) and (Mn,In) co-doped CuO samples. This could be attributed to the formation of large amounts of antiferromagnetic impurities and phase segregation in the samples. Valence state assessment showed that Mn is present in the 2+ valence state, eliminating the possibility of a double exchange interaction mechanism in this system.

(3) Various transition metal ions, such as Mn, Fe, Cr, and Ni, were doped into In_2O_3 and indium-tin oxide (ITO). In contrast to the reported data, our Fe doped In_2O_3 samples were paramagnetic. Paramagnetism was also observed in Cr doped In_2O_3 . Mn doped

In_2O_3 samples were insulators with a Curie temperature of 46 K, while Mn doped ITO samples were typical semiconductors with the same Curie temperature. Furthermore, these samples showed a large positive MR effect below the ferromagnetic transition temperature, reaching 20% at a temperature of 5 K. Ni doped In_2O_3 and ITO samples were also found to be ferromagnetic at room temperature. Electrical transport properties, though, were different in nature. Ni doped In_2O_3 was found to be a typical semiconductor, while the electrical conductivity of Ni doped ITO was found to be characteristic of metallic materials.

(4) (Fe,Mn) co-doped In_2O_3 and ITO samples were ferromagnetic at room temperature, being both conducting and insulating depending on the host semiconductor. The change in lattice parameter a was very dependent on the ratio of Mn to Fe in the system, with decrease in lattice parameter a as Fe content increased. The maximum saturation magnetization was found for an $\text{In}_{1.80}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{O}_3$ sample, which reached $0.35 \mu_B/(\text{Mn,Fe})$ ions at a temperature of 300 K. (Mn,Fe) co-doped In_2O_3 samples were insulating at room temperature, while (Fe,Cr) co-doped In_2O_3 samples were both conducting and ferromagnetic at room temperature. In addition, (Fe,Cr) co-doped samples showed a large positive MR effect, *i.e.* 5% at 5 K. On the contrary, despite being good conductors, (Mn,Fe) co-doped ITO samples did not exhibit similar MR features.

(5) (RE,Fe) co-doped In_2O_3 polycrystalline samples were semiconducting and showed giant positive magnetoresistance at 5 K. The obtained magnetoresistance in (Eu,Fe) co-doped In_2O_3 reached 80 % at 5 K. This value is the largest reported MR value for any diluted magnetic semiconductor. In addition (RE,Fe) co-doped samples showed clear ferromagnetic hysteresis behavior at 300 K. TEM studies of these samples revealed that particles are well formed and are about 100 nm in size.

Based on the results, among the transition metal doped oxide semiconductors studied, In_2O_3 and ITO are the most promising candidates for diluted semiconductor materials with possible practical applications in spintronic devices.

Contents

Introduction	2
Chapter 1. Literature review	
1. Introduction.....	7
1.1. Semiconductor materials.....	8
1.2. Basic principles of semiconductivity	9
1.2.1. Band structure of semiconductors.....	10
1.2.2. Doping of semiconductors	11
1.2.3. Charge transport in semiconductors.....	13
1.2.4. Hall Effect	15
1.3. Magnetism and magnetic materials	16
1.3.1. Spin and orbital states of the electron, Brillouin function	17
1.3.2. Magnetically ordered states	22
1.4. Spintronics: concept, materials, and applications.....	25
1.5. Progress in recent research on DMS materials	28
1.5.1. Ferromagnetism in oxide semiconductors	29
1.5.2. Transition metal doped oxide semiconductors.....	32
Chapter 2. Experimental techniques and procedures	
2. Introduction.....	45
2.1. Fabrication of samples, experimental procedures, and chemicals	46
2.2. Equipment for experimental work	53

2.2.1. Structural and physical characterization of samples	53
2.2.2. Electric and magnetotransport characterizations	55
2.2.3. Magnetic measurements.....	57
2.2.4. XANES for valence determination	58

Chapter 3. Transition metal doped ZnO

3. Introduction.....	60
3.1. Experiments	61
3.2. Results and discussion	63
3.2.1. Phase formation and purity of TM-doped ZnO	63
3.2.2. Magnetic properties of TM-doped ZnO.....	76
3.2.3. The spin state assessment of Co ions: classical Curie-Weiss law versus modified Curie-Weiss law.....	85
3.2.4. Co valence state	93
3.3. Summary	94

Chapter 4. Transition metal doped In₂O₃ and ITO

4. Introduction.....	96
4.1. Experiments	97
4.2. Results and discussion	98
4.2.1. Transition metal doped In ₂ O ₃	99
4.2.1.1. Structural characterization.....	99
4.2.1.2. Morphology and chemical composition.....	105

4.2.1.3. Magnetic properties of TM doped In ₂ O ₃	108
4.2.1.4. Transport properties of TM doped In ₂ O ₃	116
4.2.1.5. Transition metal valence state	120
4.2.2. Transition metal doped ITO	121
4.2.2.1. Structural characterization.....	122
4.2.2.2. Morphology and chemical composition	124
4.2.2.3. Magnetic properties of TM doped ITO	127
4.2.2.4. Transport properties of TM doped ITO.....	131
4.2.3. <i>Rare earth</i> and Fe co-doped In ₂ O ₃	136
4.3. Summary	142

Chapter 5. Effects of TM doping into CuO

5. Introduction.....	144
5.1. Experiments	145
5.2. Results and discussion	146
5.2.1. Structural characterization of TM doped CuO.....	146
5.2.2. Morphology and chemical composition.....	151
5.2.3. Magnetic properties.....	152
5.2.4. Valence state studies	157
5.3. Summary	159

Chapter 6. Conclusions and recommendations

6.1. Conclusions.....	160
-----------------------	-----

6.2. Further work.....	163
Bibliography	165
List of own publications	180

List of Figures

1.1.	Band structure of a) an insulator, b) a semiconductor, and c) a conductor....	11
1.2.	Effect of a magnetic field on the energy levels of the two electron states with $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$	20
1.3.	Magnetization M of several paramagnetic salts containing Gd^{3+} , Fe^{3+} , and Cr^{3+} plotted versus $\frac{\mu_0 H}{T}$	22
1.4.	Summary of the temperature dependence of the magnetization M and the magnetic susceptibility χ or reciprocal susceptibility χ^{-1} in various types of magnetic materials.....	25
1.5.	Schematic view of a magnetic random access memory (MRAM).	27
1.6.	A schematic representation of magnetic percolation in an oxide based diluted magnetic semiconductor.	31
1.7.	Crystal structure of ZnO.	33
1.8.	Observation of room temperature ferromagnetism in Mn-doped ZnO thin films.	34
1.9.	Schematic illustration of the effect of interstitial Zn on magnetic properties and $M-H$ loops for “FM switched on” and “FM switched off” states.	37
1.10.	ZFC and FC curves of Mn-doped CuO. Inset shows reciprocal magnetization as a function of temperature.	39
1.11.	Observation of RT ferromagnetism in Mn-doped Cu_2O	40
1.12.	Crystal structure of In_2O_3	41
1.13.	Anomalous Hall Effect in Cr-doped ITO.....	43
2.1.	Fabrication of polycrystalline samples via the conventional solid state synthesis technique.....	48
2.2.	Sample fabrication process using “rapid oxalate” decomposition technique.	49
2.3.	A schematic view of the experimental procedures.	50

2.4.	The families of samples that were characterized by various structural, electric and magnetic properties measurements.....	51
2.5.	The process of photoelectron scattering, and identification of the XANES region in the XAS spectrum.	59
3.1.	Heating times and temperatures applied during a) calcination, b) “rapid oxalate” decomposition, and c) sintering of the samples.....	62
3.2.	a) X-ray diffraction patterns of $Zn_{1-x}Co_xO$ samples. Impurity phase Co_3O_4 is indicated by \boxtimes . b) Dependence of lattice parameters a and c on Co content (x). Inset represents unit cell volume (V) as a function of Co content (x).	64
3.3.	X-ray diffraction patterns of $Zn_{1-x-y}Co_xMg_yO$ prepared by a conventional solid state synthesis technique. MgO and CoO impurities are indicated by \boxtimes and \blacklozenge , respectively.	66
3.4.	X-ray diffraction patterns of $Zn_{1-x-y}Co_xMg_yO$ samples prepared by a “rapid oxalate” decomposition technique. MgO and CoO impurities are indicated by \boxtimes and \blacklozenge , respectively.	67
3.5.	Lattice parameters a and c versus doping level for $Zn_{1-x-y}Co_xMg_yO$ samples prepared by a conventional solid state synthesis.....	68
3.6.	Lattice parameters a and c versus doping level for $Zn_{1-x-y}Co_xMg_yO$ samples prepared by a “rapid oxalate” decomposition technique.....	68
3.7.	X-ray diffraction patterns of $Zn_{1-y}Co_{0.15}Mg_yO$ prepared by the “rapid oxalate” synthesis technique.	70
3.8.	Dependence of lattice parameters a and c on the Mg doping level (y) for $Zn_{1-y}Co_{0.15}Mg_yO$ samples.	71
3.9.	a) X-ray diffraction patterns for $Zn_{1-x}Co_{0.075}In_xO$ samples prepared by the “rapid oxalate” synthesis technique. b) Dependence of lattice parameters a and c on indium content (x) for $Zn_{1-x}Co_{0.075}In_xO$ samples. Inset shows unit cell volume (V) versus (x).	72
3.10.	Rietveld refinement pattern for $Zn_{0.91}Co_{0.075}In_{0.015}O$ sample.....	73
3.11.	Electrical resistivity (ρ) as a function of indium content (x) for $Zn_{1-x}Co_{0.075}In_xO$ samples.....	76

3.12.	Dependence of a) molar magnetic susceptibility (χ) and b) inverse molar magnetic susceptibility ($1/\chi$) on temperature (T) for $Zn_{1-x}Co_xO$ samples.....	77
3.13.	Magnetization (M) versus applied magnetic field (H) for $Zn_{1-x}Co_xO$ samples at 10 K.....	78
3.14.	a) Molar magnetic susceptibility (χ) and b) inverse molar magnetic susceptibility ($1/\chi$) as a function of temperature (T) for $Zn_{1-x-y}Co_xMg_yO$ samples.....	80
3.15.	Magnetization (M) as a function of applied magnetic field (H) at 10 K for $Zn_{1-x-y}Co_xMg_yO$ samples.....	81
3.16.	a) Molar magnetic susceptibility (χ) and b) inverse molar magnetic susceptibility ($1/\chi$) versus temperature (T) of $Zn_{1-y}Co_{0.15}Mg_yO$ samples.....	82
3.17.	Dependence of magnetization (M) on applied magnetic field (H) at 10 K of $Zn_{1-y}Co_{0.15}Mg_yO$ samples.....	83
3.18.	Dependences of a) molar magnetic susceptibility (χ), b) inverse molar magnetic susceptibility ($1/\chi$) on temperature (T), and c) magnetization (M) as a function of applied magnetic field (H) at 10 K for $Zn_{1-x}Co_{0.075}In_xO$ samples.....	84
3.19.	Application of Curie-Weiss fitting to the $1/\chi$ curve for $Zn_{0.83}Co_{0.17}O$ sample.....	87
3.20.	Spin states and electronic configurations of Co^{2+} ion in tetrahedral crystal field splitting. LS – low spin state; HS – high spin state.....	89
3.21.	Inverse molar magnetic susceptibility ($1/\chi$) versus temperature (T) of $Zn_{1-x}Co_xO$ samples. The curves were fitted according to the Curie-Weiss law.....	91
3.22.	XANES spectra for a) $Zn_{1-x}Co_xO$ and b) $Zn_{1-y}Co_{0.15}Mg_yO$ samples. Spectra of reference samples for Co^{2+} and Co^{3+} are also shown.....	93
4.1.	X-ray diffraction pattern of $In_{2-x}TM_xO_3$ ($x = 0.1$) samples. The most intense peaks from NiO and Cr_2O_3 impurities are indicated with \diamond	100

4.2.	Dependence of lattice parameter a on the ionic radius (r_i) of the transition metal ion in $\text{In}_{2-x}\text{TM}_x\text{O}_3$ ($x = 0.1$) samples.	101
4.3	X-ray diffraction patterns of $\text{In}_{1.90}\text{Mn}_{0.10}\text{O}_3$ samples prepared in different atmospheres.	102
4.4.	Rietveld refinement of x-ray diffraction pattern for sample with $x = 0.08$. Insets: right shows a magnified view of the Rietveld refinements for samples with different x ; left shows the dependence of lattice parameter a on the Mn content x	104
4.5.	SEM micrographs of a) $\text{In}_{1.9}\text{Mn}_{0.1}\text{O}_3$, b) $\text{In}_{1.9}\text{Fe}_{0.1}\text{O}_3$, c) $\text{In}_{1.8}\text{Mn}_{0.08}\text{Fe}_{0.12}\text{O}_3$, and d) $\text{In}_{1.8}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{O}_3$ samples.	106
4.6.	Magnetic susceptibility (χ) versus temperature (T) of $\text{In}_{1.9}\text{TM}_x\text{O}_3$ samples with TM = (a) Mn, (b) Fe, (c) Cr, and (d) Ni. Insets represent the inverse magnetic susceptibility ($1/\chi$) data vs. (T).	109
4.7.	Magnetization (M) versus applied magnetic field (H) of $\text{In}_{1.9}\text{TM}_{0.1}\text{O}_3$ samples at a) 300 K; b) 10 K.	111
4.8.	a) Dependence of magnetization (M) on temperature (T) for various TM doped In_2O_3 samples; b) magnetization (M) vs. applied magnetic field (H) for $\text{In}_{1.8}\text{Fe}_{0.1}\text{Cr}_{0.1}\text{O}_3$ sample. Inset shows an enlargement of the selected area of the M - H loops.	112
4.9.	Molar magnetic susceptibility (χ) as a function of temperature (T) for $\text{In}_{2-x-y}\text{Mn}_x\text{Fe}_y\text{O}_3$ samples.	113
4.10.	Magnetization (M) vs. applied magnetic field (H) for $\text{In}_{2-x-y}\text{Mn}_x\text{Fe}_y\text{O}_3$ samples at a) 10 K; b) 300 K.	115
4.11.	Electrical resistivity (ρ) as a function of temperature (T) for various TM-doped In_2O_3 samples.	116
4.12.	Fittings of logarithm of electrical resistivity (ρ) versus temperature (T) for TM doped In_2O_3 samples: (a) NNH; (b) VRH conduction models.	118
4.13.	Magnetoresistance (MR) at various temperatures for $\text{In}_{1.8}\text{Fe}_{0.1}\text{Cr}_{0.1}\text{O}_3$ sample.	119

4.14.	X-ray absorption spectra for a) Mn <i>L</i> -edge and b) Fe <i>L</i> -edge in $\text{In}_{1.90}\text{TM}_{0.10}\text{O}_3$ samples.	120
4.15.	X-ray diffraction patterns of $\text{In}_{1.84}\text{TM}_{0.1}\text{Sn}_{0.06}\text{O}_3$ samples.	122
4.16.	a) X-ray diffraction patterns for $\text{In}_{1.80-x}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{Sn}_x\text{O}_3$ samples; b) dependence of lattice parameter <i>a</i> on Sn content (<i>x</i>).	123
4.17.	SEM images of a) $\text{In}_{1.84}\text{Mn}_{0.1}\text{Sn}_{0.06}\text{O}_3$ and b) $\text{In}_{1.84}\text{Fe}_{0.1}\text{Sn}_{0.06}\text{O}_3$ samples	125
4.18.	TEM image of $\text{In}_{1.74}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{Sn}_{0.06}\text{O}_3$ sample.	125
4.19.	SEM pictures of In_2O_3 single crystals taken from a) top and b) side.	126
4.20.	a) SEM picture of Mn-Fe-Sn “spheres”; b) x-ray diffraction pattern for the same sample.	127
4.21.	a) Magnetization (<i>M</i>) versus temperature (<i>T</i>) for TM doped ITO samples. The inset shows a magnified view of the bottom part of the graph; b) Molar magnetic susceptibility (χ) vs. temperature (<i>T</i>) for Mn doped ITO samples.	128
4.22.	Magnetization (<i>M</i>) vs. temperature (<i>T</i>) for $\text{In}_{1.80-x}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{Sn}_x\text{O}_3$ samples.	129
4.23.	Magnetization (<i>M</i>) as a function of temperature (<i>T</i>) for a) Mn-doped ITO at 10 K; b) (Mn,Cr) co-doped ITO at 300 K. Inset shows the dependence of the saturation magnetization (<i>M_s</i>) on Sn content (<i>x</i>).	130
4.24.	Dependence of electrical resistivity (ρ) on Sn content (<i>x</i>) at 300 K for $\text{In}_{1.80-x}\text{Mn}_{0.12}\text{Fe}_{0.08}\text{Sn}_x\text{O}_3$ samples.	131
4.25.	Dependence of electrical resistivity (ρ) on temperature (<i>T</i>) for a) TM doped ITO samples; b) Ni-doped ITO sample.	132
4.26.	Magnetoresistance (MR) measured at various temperatures for $\text{In}_{1.84}\text{Mn}_{0.1}\text{Sn}_{0.06}\text{O}_3$ sample.	135
4.27.	X-ray diffraction patterns for $\text{In}_{1.98-x}\text{Fe}_{0.02}\text{RE}_x\text{O}_3$ samples. InREO_3 and RE_2O_3 impurities are indicated by \diamond	137
4.28.	a) Molar magnetic susceptibility (χ) as a function of temperature (<i>T</i>) for $\text{In}_{1.98-x}\text{Fe}_{0.02}\text{RE}_x\text{O}_3$ samples; b) M-H loops at 300 K for the same samples.	138

4.29.	a) Electrical resistivity (ρ) vs. temperature (T) for $\text{In}_{1.93}\text{Fe}_{0.02}\text{RE}_{0.05}\text{O}_3$ samples; magnetoresistance (MR) measured at various temperatures for b) $\text{In}_{1.93}\text{Fe}_{0.02}\text{Eu}_{0.05}\text{O}_3$, and c) $\text{In}_{1.93}\text{Fe}_{0.02}\text{Nd}_{0.05}\text{O}_3$; d) illustration of negative MR in $\text{In}_{1.93}\text{Fe}_{0.02}\text{Eu}_{0.05}\text{O}_3$	140
4.30.	TEM micrographs of a) (Eu,Fe) co-doped and b) (Nd,Fe) co-doped In_2O_3 sample particles. TEM-EDS spectra for the corresponding particles are shown in the bottom parts of the figure.....	141
5.1.	X-ray diffraction patterns for $\text{Cu}_{1-x}\text{Mn}_x\text{O}$ samples. $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ impurities are identified with \diamond	147
5.2.	Dependence of lattice parameters a) a , b) b , c) c , and d) the β angle on Mn doping content (x) in $\text{Cu}_{1-x}\text{Mn}_x\text{O}$ samples.....	148
5.3.	X-ray diffraction patterns of $\text{Cu}_{0.9-x}\text{Mn}_{0.1}M_x\text{O}$, where $M = \text{Zn}(\text{In})$. Characteristic CuO peaks are indicated by (*). In and Zn based impurities are indicated by (\diamond) and (\blacklozenge), respectively.....	149
5.4.	SEM micrographs of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{O}$ prepared at a) 950 °C, b) 970 °C; and $\text{Cu}_{0.85}\text{Mn}_{0.1}\text{In}_{0.05}\text{O}$ prepared at c) 950 °C, d) 970 °C.....	152
5.5.	Molar magnetic susceptibility (χ) as a function of temperature (T) for $\text{Cu}_{1-x}\text{Mn}_x\text{O}$ samples.....	153
5.6.	Dependence of magnetization (M) on the applied magnetic field (H) at 10 K for $\text{Cu}_{1-x}\text{Mn}_x\text{O}$ samples.....	155
5.7.	a) Molar magnetic susceptibility (χ) as a function of temperature (T) for some “single” and “double” doped CuO samples. Inset shows magnified view of χ - T curves at low temperatures; b) Magnetization (M) vs. applied magnetic field (H) for “single” and “double” doped CuO samples.....	157
5.8.	XANES spectra for $\text{Cu}_{1-x}\text{Mn}_x\text{O}$ samples.....	158

List of Tables

1.1.	List of some common semiconductors.	8
1.2.	Electronic properties of various transparent oxide semiconductors, where ρ , n , μ , and E_g denote resistivity, carrier density, mobility, and energy gap at room temperature, respectively.	29
2.1.	The list of reagents used in this study.	52
3.1.	Ionic radii of various ions used in this study.	63
3.2.	Crystallographic data for $Zn_{1-x}Co_{0.075}In_xO$ samples calculated by the Rietveld method.	74
3.3.	Chemical compositions of the samples as determined by SEM-EDS spot analysis. The raw values are normalized by the Co content.	75
3.4.	Calculated Curie-Weiss temperatures (Θ) and effective magnetic moments (μ_{eff}) of Co ions in $Zn_{0.93}Co_{0.17}O$ as a function of the temperature range (T) (Fig. 3.19) used for the Curie-Weiss fittings.	88
3.5.	The calculated Curie-Weiss temperatures (Θ) and effective magnetic moment (μ_{eff}) per Co ion for (Mg,Co) and (In,Co) co-doped samples.	92
4.1.	Chemical compositions of the samples as determined by SEM-EDS spot analyses and aerial element mappings.	106
4.2.	Θ , μ_{eff} , and estimated spin states of magnetic ions obtained from modified Curie-Weiss law fits on the $1/\chi(T)$ curves shown in Fig. 4.6.	110
5.1.	Lattice parameters a , b , and c for $Cu_{0.91}Mn_{0.09}O$, $Cu_{0.85}Mn_{0.1}In_{0.05}O$, and $Cu_{0.85}Mn_{0.1}Zn_{0.05}O$ samples.	150
5.2.	Effective magnetic moments (μ_{eff}), Curie-Weiss temperatures (Θ), and Mn spin states in $Cu_{1-x}Mn_xO$ samples.	154

List of Symbols and Abbreviations

A	Cross section area	Fig	Figure
Å	Angstrom	FM	Ferromagnetism
AC	Alternating Current	g	Gram
B, \vec{B}	Magnetic induction	g_e	Spectroscopic splitting factor
$B_J(y)$	Brillouin function	g_J	Landé spectroscopic factor
BMP	Bound magnetic polaron	GM	Granulated Metal
C	Curie constant; Celsius	GMR	Giant Magnetoresistance
cm	Centimetre	h	Hour
DC	Direct Current	\vec{H}, H	Magnetic field
DMS	Diluted Magnetic Semiconductor	HS	High Spin
DS	Degenerate Semiconductor	i	Initial state of carrier hopping
e	Electron	I	Current
<i>e.g.</i>	Exempli gratia, in Latin meaning “for example	<i>i.e.</i>	Id est, in Latin meaning “that is”
EDS	Energy Dispersive Spectroscopy	ICDD	International Centre for Diffraction Data
E_F	Fermi energy	IS	Intermediate Spin
E_g	Energy gap at room temperature	ITO	Indium Tin Oxide
emu	Electro-magnetic unit	j	Final state of carrier hopping
Eq	Equation	\vec{J}	The total angular momentum
<i>et al.</i>	Et al ii, in Latin meaning “and others”	K	Kelvin
eV	Electronvolt	k, k_B	Boltzmann constant
exp	Exponential	l	The orbital angular momentum quantum number
FC	Field Cooled	\vec{l}_i	The orbital angular momentum

L	Distance between voltage contacts	PC	Personal Computer
\vec{L}	The total orbital angular momentum	PPMS	Physical Property Measurement System
LED	Light Emitting Diode	R	Electrical resistance
LS	Low Spin	RE	Rare Earth
m	Mass	r_i	Ionic radius
M	Magnetization	r_{ij}, R	Distance between “ i ” and “ j ” in carrier hopping model
min	Minute	R_s	Anomalous Hall coefficient
m_l	The magnetic quantum number	RT	Room Temperature
mm	Millimetre	R_o	Ordinary Hall coefficient
MPMS	Magnetic Property Measurement System	\vec{s}_i	The spin angular momentum
MR	Magnetoresistance	S	Siemens
MRAM	Magnetic Random Access Memory	\vec{S}	The total spin angular momentum
m_s	The spin quantum number	sec	Second
n	The principal quantum number, charge carrier density	SEM	Scanning Electron Microscopy
N	The number of atoms	SRRC	Synchrotron Radiation Research Centre
N_A	Avogadro’s number	T	Temperature
$N(E_F)$	Density of states at Fermi energy	T	Tesla
NNH	Nearest Neighbor Hopping	T_C	Curie temperature
Oe	Oersted	TCR	Temperature Coefficient of Resistivity
PC	Personal Computer	TEM	Transmission Electron Microscopy
PPMS	Physical Property Measurement System	TM	Transition Metal

T_N	Néel temperature	$\Delta\rho$	Difference of electrical resistivity
V	Volt	μ	Charge carrier mobility, micro
V	Voltage, Volume	$\vec{\mu}$	Magnetic moment
VRH	Variable Range Hopping	μ_B	Bohr magneton
W	Hopping energy	μ_{eff}	Effective magnetic moment
wt%	Weight percent	$\vec{\mu}_l$	Associated magnetic moment of an electron with an orbital angular momentum
XAFS	X-ray Absorption Fine Structure	μ_{lz}	Projection of magnetic moment along direction of applied magnetic field
XANES	X-ray absorption near band edge spectroscopy	$\vec{\mu}_s$	Associated magnetic moment of an electron with spin angular momentum
XAS	X-ray absorption spectroscopy	μ_0	Magnetic permeability
XPS	X-ray Photoemission Spectroscopy	2θ	Diffraction angle in x-ray diffraction
XRD	X-ray Diffraction	Θ	Curie-Weiss temperature
ZFC	Zero Field Cooled	ρ	Electrical resistivity
α	Wave function decay factor	ρ_H	Electrical resistivity under applied magnetic field
χ	Magnetic susceptibility	ρ_{xy}	Hall resistivity
$\chi^{-1}, (1/\chi)$	Reciprocal magnetic susceptibility	ρ_0	Electrical resistivity in zero magnetic field
χ_0	Temperature independent magnetic susceptibility	σ	Electrical conductivity

Ω	Ohm
$^{\circ}$	Degree
$^{\circ}\text{C}$	Degrees Celsius
\hbar	Plank constant