

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Hybrid Organic-Inorganic Layered Electronic Materials

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Physics

at Massey University, Manawatu Campus

New Zealand.

Islah-u-din

2012

Abstract

Hybrid organic-inorganic materials combine distinct features of organic and inorganic components into single molecular frameworks that exhibit tunable electronic, optical and magnetic properties. An extending layered network is formed by covalently bound layers of inorganic materials that are electronically coupled by organic components. A control on the stacking orientation of these layers can help tailor the structural, physical and chemical properties of resulting compounds.

This thesis presents an investigation of the synthesis, characterization and effects of doping, primarily by ion-implantation, on structural, chemical and physical properties of transition-metal oxide based organic-inorganic hybrid materials. These materials were synthesized and characterized by a variety of experimental techniques. The crystal structures of these compounds were probed by powder and single-crystal X-ray diffraction while various other techniques such as Raman spectroscopy, X-ray photoelectron spectroscopy, magnetic and resistivity measurements were applied to examine the chemical and physical properties of these materials. The crystal structure of these materials consists of infinite layers of transition metal oxides interlinked by organic ligands. The organic-ligands are aligned so as to define small cages within these structures, potentially, to accommodate metal ions. Intercalation of alkali-metal atoms within these cages brings about important alterations in the structural, chemical and physical properties of these materials. The presence of intercalated species was confirmed by single-crystal X-ray diffraction and X-ray photoelectron spectroscopy while spectral changes observed from Raman measurements and a significant reduction in electrical resistance of implanted materials refer to charge carrier-injection into the conduction band.

Significant changes in structure and physical properties of these materials were observed by increasing the number of atoms in ligand tethers while introduction of additional metal atoms, by in-situ doping, in the inorganic oxide layers, leads to strong antiferromagnetic interactions in otherwise diamagnetic materials. These results demonstrate the possibilities of exploiting the self-assembly of organic and inorganic precursors to realize the potential applications these materials have to offer.

Preface

Some of the results described in this thesis have been published in the following international journal articles. Few other articles are in preparation.

1. Islah-u-din, S. V. Chong, S. G. Telfer, J. Kennedy, G. B. Jameson, M. R. Waterland and J. L. Tallon, “Influence of Doping on Hybrid Organic-Inorganic $\text{WO}_3(4,4'$ -bipyridyl) $_{0.5}$ Materials”, *The Journal of Physical Chemistry C*, 2012, 116, 3787-3792.
2. Islah-u-din, M. R. Fox, H. Martin, G. J. Gainsford, J. Kennedy, A. Markwitz, S. G. Telfer, G. B. Jameson and J. L. Tallon, “Synthesis and Structure of Na^+ -intercalated $\text{WO}_3(4,4'$ -bipyridyl) $_{0.5}$ ”, *Chemical Communications*, 2010, 46, 4261-4263.

These results were also presented at the following conferences

1. 2nd International Advances in Applied Physics and Materials Science, Antalya, Turkey, April 26 – 29, 2012. [Oral presentation]
2. JAIST International School on Emerging Nanotechnologies, Kanazawa, Japan, March 26 – 29, 2012. [Poster presentation]
3. New Zealand Institute of Physics Conference, Wellington, New Zealand, October 17 – 19, 2011. [Oral presentation]
4. Hybrid Materials: 2nd International Conference on Multifunctional, Hybrid and Nanomaterials, Strasbourg, France, March 6 – 10, 2011. [Poster presentation]

Acknowledgements

I must thank my supervisors Dr. Mark R. Waterland, Dr. Shane G. Telfer and Dr. Jeffery L. Tallon for all their support and guidance towards completion of this study.

I am very grateful to Prof. Geoffrey B. Jameson for his untiring efforts in teaching me X-ray crystallography and for all his help in solving very complex crystal structures. Despite his very busy schedule he has always been very kind to spare time for thoughtful discussions on different aspects of this project. I really appreciate his cooperation.

Thanks a lot to Dr. Shen V. Chong (Industrial Research Ltd.) for his help with so many experiments, especially for doing magnetic measurements.

Many thanks to Dr. John V. Kennedy and Dr. Vivian Fang (GNS Science, Lower Hutt) for organising ion-implantation experiments.

I am indebted to Higher Education Commission, Pakistan for providing me a doctoral scholarship to study in New Zealand. I would never have imagined doing a PhD without this scholarship. I am also very thankful to MacDiarmid Institute of Nanotechnology for providing partial financial support and access to numerous experimental facilities across the New Zealand. Many Thanks to Institute of Fundamental Sciences for providing financial support towards conference travel.

A big thanks to Pakistani community in Palmerston North, especially Dr. Zulfiqar H. Butt for their support during last five years. Many thanks to all my friends and well wishers for their great company.

Finally, I am very thankful to all my family who have to live all these years without me.

Contents

Abstract	ii
Preface	iii
Acknowledgements	iv
Contents	v
List of Figures	viii
List of Tables	xvi
1 Introduction	1
1.1 Electron Physics in Correlated Oxide Systems.....	2
1.1.1 Jahn-Teller Effect.....	4
1.1.2 Mott Insulators	5
1.1.3 Colossal Magnetoresistance.....	6
1.1.4 High Temperature Superconductivity.....	7
1.2 Hybrid Organic-Inorganic Layered Electronic Materials	10
1.2.1 Definition: Hybrid Materials.....	10
1.2.2 Origins of Hybrid Materials.....	11
1.2.3 Properties and Applications of Hybrid Materials	13
1.2.4. Classification of Hybrid Materials.....	19
1.3 Aims and objectives.....	27
2 Experimental Techniques	29
2.1 Hydrothermal Synthesis.....	29
2.2 Ion-Implantation	31
2.2.1 Ion Implantation Process.....	32
2.2.2 Ion-Implantation Applications	35
2.3 Characterization Techniques.....	36
2.3.1 X-ray Diffraction	36

2.3.2 X-ray Photoelectron Spectroscopy	41
2.3.3 Raman Spectroscopy.....	44
2.3.4. Magnetic Measurements	47
3 Synthesis, structure and physical properties of Na⁺ -intercalated WO₃ (4,4'-bipyridyl)_{0.5} hybrid material	50
3.1 Introduction.....	50
3.2 Experimental Details.....	52
3.2.1 Synthesis	52
3.2.2 Ion-Implantation	53
3.2.3 Characterization	53
3.3 X-ray Diffraction	54
3.4 Magnetic Measurements	63
3.5 Raman Measurements.....	65
3.6 Summary	69
4 Influence of doping on hybrid organic-inorganic WO₃(4, 4'-bipyridyl)_{0.5} materials	71
4.1 Introduction.....	71
4.2 Experimental Details.....	72
4.2.1 Synthesis	72
4.2.2 Ion-Implantation	75
4.2.3 Characterization	75
4.3 Thick-film structure	76
4.4 Single-crystal X-ray Diffraction Studies	79
4.5 Raman Spectroscopy.....	82
4.6 X-Ray Photoelectron Spectroscopy	84
4.7 Resistivity Measurements	88
4.8 Summary	89

5 Synthesis and characterization of novel single and bimetallic layered organic-inorganic hybrid materials	90
5.1 Introduction.....	90
5.2 Experimental Details.....	92
5.2.1 Synthesis	92
5.2.2 Characterization	93
5.3 Single Crystal X-ray Diffraction.....	93
5.3.1 WO ₃ -phen and MoO ₃ -phen.....	93
5.3.2 CuMoO ₄ -phen.....	97
5.3.3 Cu ₃ Cr ₂ O ₁₀ -phen.....	99
5.4 Powder X-ray Diffraction	103
5.5 Raman Spectroscopy.....	106
5.6 Magnetic Measurements	111
5.7 Summary	114
6 Summary and Future Directions	115
6.1 Summary	115
6.2 Future prospects	118
A Bond Valence Sum Calculations	120
B Unsuccessful Synthesis	124
C X-ray Crystal Structure Data	136
References	137

List of Figures

Figure 1.1 (a) Octahedral representation of transition metal oxide. (b) Different orientations for 3d orbitals in transition metal oxides where fivefold degeneracy is lifted to two e_g [$(x^2 - y^2)$ and (z^2)] orbitals and three t_{2g} orbitals [(xy), (yz), and (zx)]. (c) Crystal field splitting.	4
Figure 1.2 Silicic skeleton of a diatom, showing complex and finely carved morphology in scanning electron microscopy.....	12
Figure 1.3 Computer enhanced Mayan warrior from Bonampak.	12
Figure 1.4 Organic-inorganic hybrid materials containing organic chromophores.	15
Figure 1.5 (a) A core-shell silica microcapsule for carrying potent chemicals. (b) Commercial Sunscreen SPF 20.....	16
Figure 1.6 Artificial hydrophobic coatings inspired by lily leaves.....	17
Figure 1.7 (a) High quality optical appearance of crystal glass. (b) Easy to recycle coloured glass bottles coated with hybrid organic-inorganic materials.....	17
Figure 1.8 ORMOCER waveguides where the hybrid coating is deposited on a flexible foil	18
Figure 1.9 (a) Pentium MCM-L/D manufactured in ORMOCER. (b) Electro-optical o/e MCM manufactured in ORMOCER.....	18
Figure 1.10 Layered structure of manganese phosphite stacking along <i>c</i> -axis with alkyldiammonium ions filling the interlayer space.....	20
Figure 1.11 A layered perovskite material.....	20
Figure 1.12 Layered structure of $KCa_2Nb_3O_{10}$ where Ca atoms (small circles) occupy the interlayer space formed by corner shared NbO_6 octahedra.	21
Figure 1.13 Octahedral symmetries as demonstrated by perovskite tungsten bronze unit cell.	22

Figure 1.14 Tungsten oxide octahedra arranged in corner-sharing configuration to form monoclinic WO_3 (above) and two layers of octahedral tungsten oxide stacked so as to reveal vacant tunnels along the z-direction (below).	23
Figure 1.15 Edge-sharing arrangement of WO_6 octahedra leads to formation of substiochiometric WO_{3-x}	24
Figure 1.16 Crystal structure of $[[\text{Ni}(2,2'\text{-bipyridyl})_2]_2\text{Mo}_4\text{O}_{14}]$	26
Figure 2.1 A stainless steel Teflon-lined autoclave used for synthesizing hybrid materials. 30	
Figure 2.2 Schematics of a typical ion-implanter.	33
Figure 2.3 A low energy ion-implanter at GNS Sciences, Lower Hutt was used for doping metal atoms into single crystals and thick films.	35
Figure 2.4 A simplified sketch of the X-ray diffractometer.	37
Figure 2.5 A pictorial illustration of Bragg's law.	37
Figure 2.6 The Rigaku spider diffractometer at Massey University, Palmerston North that was used for structural characterization of crystalline materials.	39
Figure 2.7 A powder X-ray diffractometer at Industrial Research, Lower Hutt was used for preliminary structural characterization of polycrystalline hybrid materials.	41
Figure 2.8 An explanation of basic principle of XPS.	42
Figure 2.9 The Kratos Axis UltraDLD surface-analyzing chamber at the University of Auckland that was used for XPS measurements.	43
Figure 2.10 Different light scattering techniques.	44
Figure 2.11 The LabRam instrument at Victoria University, Wellington was used for solid-state Raman measurements.	46
Figure 2.12 A simplified schematic representation of DC SQUID operation. Green stripes represent Josephson junctions.	47

Figure 2.13 A Quantum Design MPMS XL SQUID at Industrial Research Ltd. was used for magnetic characterization.	49
Figure 3.1 Crystal structure of WO ₃ -bpy. ⁷¹ Layers of corner-shared tungsten oxide octahedra are bridged by bpy ligands defining open structure channels. Tungsten atoms are shown in green, oxygen in red, nitrogen in blue and carbon in grey. Hydrogen atoms are omitted for clarity. (<i>c</i> -axis is horizontal).	51
Figure 3.2 Polymer bound thick film of WO ₃ -bpy coated on ITO glass substrate.	53
Figure 3.3 A high-resolution snapshot of WO ₃ bpy single crystal before (left) and after (right) Na ⁺ ion-implantation.	54
Figure 3.4 Powder XRD patterns demonstrate strong <i>00l</i> reflections which indicate the formation of layered structures for both forms of WO ₃ -bpy: black = pattern calculated from single-crystal XRD, red = experimental pattern of WO ₃ -bpy. The diffraction angle is for Co K α radiation. For comparison, the wavelength was changed to Co K α in the pattern calculated from single crystal structure of WO ₃ -bpy, which was determined with Cu K α radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.	55
Figure 3.5 A comparison of XRD patterns obtained from WO ₃ -bpy pellets annealed at different temperatures. A notable decrease in intensity of all the peaks is observable as temperature increases. Beyond 460 °C, this decrease in intensity becomes significant with a clear broadening in (006) and (0012) peaks suggesting the disintegration of layered structure. Intensity is measured in arbitrary units and Bragg angle in degrees.	56
Figure 3.6 A comparison of XRD patterns obtained from WO ₃ -bpy polymer bound films before and after ion-implantation. Intensity is measured in arbitrary units and Bragg angle in degrees.	57
Figure 3.7 Structural repeat unit for Na _x WO ₃ -bpy showing two WO ₅ N octahedra linked via the nitrogens on the bpy. Tungsten atoms are shown in green, oxygens in red, nitrogens in blue, carbons in grey and hydrogens in white. (<i>c</i> -axis is horizontal). Graphics using MERCURY.	60

Figure 3.8 The crystal structure of WO_3 -bpy consists of layers of corner-shared octahedral tungsten oxide bridged by bpy ligands. The colour scheme is similar to Fig. 3.7. (<i>c</i> -axis is horizontal).Graphics using DSViewPro.....	60
Figure 3.9 (a) Structural repeat unit for Na_xWO_3 -bpy showing two WO_5N octahedra linked via the nitrogens (blue) on the bpy. The intercalated Na^+ ions (yellow) are bimodally located in the cage bounded along the <i>c</i> -axis by the axial oxygens (red), as depicted in (b). A cage structure is formed by the alternating alignment of the bpy planes. The display style is changed in (b) for convenience. The colour scheme is the same for both. (<i>c</i> -axis is horizontal.) Graphics using MERCURY.	61
Figure 3.10 The crystallographic structure of Na_xWO_3 -bpy showing the inorganic WO_3N framework layers and one organic cage housing the Na^+ intercalant. Atoms are coloured as in Fig. 3.7. (Graphics using PLATON and POV-RAY).	62
Figure 3.11 ZFC magnetic measurements of WO_3 -bpy films measured at 2×10^{-4} Tesla.	64
Figure 3.12 Temperature-dependence of ZFC magnetic moment for unimplanted and Na^+ -implanted polymer-bound WO_3 -bpy films.	65
Figure 3.13 Raman spectra of pure $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. Intensity is measured in arbitrary units.	66
Figure 3.14 Raman spectra of pure bpy. Data was collected over two spectral windows ($330\text{--}1050 \text{ cm}^{-1}$ to $1050\text{--}1800 \text{ cm}^{-1}$). Intensity is measured in arbitrary units.	66
Figure 3.15 Raman spectra of powdered WO_3 -bpy. Intensity is measured in arbitrary units.	68
Figure 3.16 Raman spectra of doped and undoped polymer bound films. Intensity is measured in arbitrary units.....	69
Figure 4.1 A possible structural model for multilayer thin films of WO_3 -bpy.	73
Figure 4.2 A simplified sketch of modified layer-by-layer scheme for deposition of WO_3 -bpy on ITO.	74
Figure 4.3 An SEM image of WO_3 -bpy coated ITO using SEM reveals the formation of intergrown microcrystals.	76

Figure 4.4 Powder X-ray diffractograms of WO₃-bpy. The diffraction angle is for Co K α radiation. Evidence for the same layered structure for all the forms of WO₃-bpy: black = pattern calculated from the single-crystal structure, red = experimental pattern of bulk WO₃-bpy, blue = experimental pattern of ITO-bound WO₃-bpy. For comparison, wavelength was changed to Co K α in the pattern calculated from single crystal structure of WO₃-bpy, which was determined with Cu K α radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.....77

Figure 4.5 A comparison of powder XRD patterns obtained from WO₃-bpy films before and after ion-implantation. Intensities were enlarged in both figures. The diffraction wavelength is of Co K α . Intensity is measured in arbitrary units and Bragg angle in degrees..... 78

Figure 4.6 A comparison of powder XRD patterns calculated from single crystal XRD measurements of WO₃-bpy materials before and after ion-implantation. The diffraction wavelength is of Cu K α . Intensity is measured in arbitrary units and Bragg angle in degrees. 78

Figure 4.7 Crystal structures of WO₃-bpy before (left) and after implantation (centre, Ca²⁺ and right, K⁺). Tungsten atoms are shown in green, oxygens in red, nitrogens in blue. Yellow colour represents the sites attributed to implantation of Ca²⁺ (centre) and K⁺ (right) ions. Like Na⁺, Ca²⁺ resides disordered over two sites away from the inversion centre in the centre of the cage, while K⁺ resides at the cage centre on a crystallographic centre of inversion. Graphics using PLATON and POV-RAY..... 80

Figure 4.8 Raman spectra of WO₃-bpy before and after ion-implantation. (a) Bulk crystalline WO₃-bpy material, (b) WO₃-bpy film before implantation, (c) Na⁺-implanted WO₃-bpy film, (d) Ca²⁺-implanted WO₃-bpy film (e) K⁺-implanted WO₃-bpy film. 82

Figure 4.9 XPS scans of WO₃-bpy films before and after ion-implantation. 86

Figure 4.10 Deconvolution of XPS peaks C 1s (left) and O 1s (right) for non-implanted and implanted thick films of WO₃-bpy..... 86

Figure 4.11 Evolution of the W 4f XPS peaks upon ion-implantation. The arrows indicate the position of tungstate species with respect to the W 4f_{7/2} peak. 87

Figure 4.12 Intercalated species were detected by XPS for Ca 2 <i>p</i> , K 2 <i>p</i> and Na 1 <i>s</i> in ion-implanted WO ₃ -bpy films.	87
Figure 4.13 Temperature dependence of the resistance of WO ₃ -bpy films before and after Ca ²⁺ implantation. The inset shows the corresponding V-I curves measured at room temperature. The displayed resistances are calculated from dotted lines in the respective V-I curves.	89
Figure 5.1 A comparison of 1,10-phenanthroline (left) and 3,8-phenanthroline (right) structures.	91
Figure 5.2 Crystal repeat unit for MO ₃ -phen (where M = W or Mo). O ₂ and O ₃ have 50% occupancy for both structures making metal-oxide ratio to 1:3. Hydrogen atoms are omitted for clarity.	93
Figure 5.3 A comparison of ligand-packing for WO ₃ -bpy (left) and WO ₃ -phen (right) structures. It can be noted that the cavity between apical oxygens is much smaller for WO ₃ -phen as compared to that of WO ₃ -bpy. Colour scheme is similar to Fig.5.2.	96
Figure 5.4 Crystal structure of CuMoO ₄ -phen. A structural motif (left) and a complete structure (right) is generated by bimetallic layers of edge-shared copper oxide octahedra and corner shared molybdenum oxide tetrahedra in the <i>ab</i> -plane while ligands interconnect the inorganic layers to form a 3D covalent framework. Hydrogen atoms are omitted for clarity. Copper is displayed in cyan, molybdenum in pink, oxygen in red, nitrogen in blue and carbon in grey.	97
Figure 5.5 Coordination geometries for Mo (left) and Cu (right) sites. Both Cu(3) and Cu(4) have similar six coordination. Although both Mo(1) and Mo(2) are four coordinated, the coordination at Mo(1) is defined by four bridging oxo while for Mo(2) it is composed of three bridging oxo and a terminal group. Colour scheme similar to Fig. 5.4.	98
Figure 5.6 Crystal repeat unit of Cu ₃ Cr ₂ O ₁₀ -phen (left) and complete structure (right). Colour scheme is same in both figures. Hydrogens and disordered carbon atoms are removed from right side figure for clarity.	99

Figure 5.7 A metal-oxide inorganic layer of $\text{Cu}_3\text{Cr}_2\text{O}_{10}$ -phen demonstrating coordination geometries of the three metal ion sites.....	101
Figure 5.8 Powder X-ray diffractograms for WO_3 -phen, MoO_3 -phen, CuMoO_4 -phen and $\text{Cu}_3\text{Cr}_2\text{O}_{10}$ -phen. The diffraction angle is for Co $K\alpha$ radiation. The intensities were scaled in both figures for better comparison. Intensity is measured in arbitrary units and Bragg angle in degrees.	104
Figure 5.9 A comparison of experimental and calculated powder X-ray patterns for WO_3 -phen. For comparison, the wavelength was changed to Co $K\alpha$ in the pattern calculated from the single crystal structure of WO_3 -phen, which was determined with Cu $K\alpha$ radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.	104
Figure 5.10 A comparison of experimental and calculated powder X-ray patterns for MoO_3 -phen. For comparison, the wavelength was changed to Co $K\alpha$ in the pattern calculated from the single crystal structure of MoO_3 -phen, which was determined with Cu $K\alpha$ radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.	105
Figure 5.11 A comparison of experimental and calculated powder X-ray patterns for CuMoO_4 -phen. For comparison, the wavelength was changed to Co $K\alpha$ in the pattern calculated from the single crystal structure of CuMoO_4 -phen, which was determined with Cu $K\alpha$ radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.	105
Figure 5.12 A comparison of experimental and calculated powder X-ray patterns for $\text{Cu}_3\text{Cr}_2\text{O}_{10}$ -phen. For comparison, the wavelength was changed to Co $K\alpha$ in the pattern calculated from the single crystal structure of $\text{Cu}_3\text{Cr}_2\text{O}_{10}$ -phen, which was determined with Cu $K\alpha$ radiation. Intensity is measured in arbitrary units and Bragg angle in degrees.	106
Figure 5.13 A comparison of Raman spectra of WO_3 -phen and WO_3 -bpy. Intensity is measured in arbitrary units.....	107
Figure 5.14 Experimental and calculated Raman spectra of 1,10-phenanthroline. Experimental spectrum was recorded in solid state with 633 nm excitation. Intensity is measured in arbitrary units.....	108
Figure 5.15 Theoretical spectrum of phen calculated using Gaussian09. Figure was generated using GaussView 5. Intensity is measured in arbitrary units.....	108

Figure 5.16 Raman spectra of MoO ₃ -phen and MoO ₃ -bpy. Intensity is measured in arbitrary units.....	109
Figure 5.17 A comparison of Raman spectra obtained from CuMoO ₄ , CuMoO ₄ -bpy and CuMoO ₄ -phen. Despite the different nature of ligands, the position of 929 cm ⁻¹ remains unchanged in all three compounds which reflects the strong influence of terminal oxo groups. Intensity is measured in arbitrary units.	110
Figure 5.18 Temperature-dependent volume susceptibility measurements recorded at different applied fields for WO ₃ -phen (left) and MoO ₃ -phen (right).	112
Figure 5.19 Volume magnetic susceptibility of CuMoO ₄ -phen measured at different applied fields.....	113
Figure 5.20 Curie-Weiss Fitting to high-temperature susceptibility data of CuMoO ₄ -phen.	113
Figure 5.21 Temperature-dependent χT plots for CuMoO ₄ -phen recorded at different applied fields.....	114

List of Tables

Table 3.1 Selected X-ray crystallography details for WO ₃ -bpy.....	59
Table 4.1 Selected single-crystal X-ray diffraction data collection and refinement details of implanted and non-implanted WO ₃ -bpy	81
Table 5.1 Selected crystallographic and refinement details for WO ₃ -phen and MoO ₃ -phen hybrids.....	95
Table 5.2 Selected crystallographic and refinement details for CuMoO ₄ -phen and Cu ₃ Cr ₂ O ₁₀ -phen hybrids.....	102
Table A1: Selected Cu(2)–O bond distances. Mathematical transformations used to generate symmetrically equivalent atoms: $g = 1-x,-y,-z$	121
Table A2: Selected Cu(1)–O bond distances. Mathematical transformations used to generate symmetrically equivalent atoms: $a = -1+x,y,z$; $b = -1+x,1+y,-1+z$; $e = -x,-y,-z$	122
Table A3: Selected Cr(3)–O bond distances.....	123
Table B1 Details of unsuccessful synthesis.	125