

**SYNTHESIS AND CHARACTERIZATION
OF UNSUPPORTED COPPER SULFIDE FOR MERCURY
TRAPPING IN AQUEOUS SYSTEM**

YAP PEI LAY

**DISSERTATION SUBMITTED IN FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2012

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **YAP PEI LAY**

(I.C No: **850429145802**)

Registration/Matric No: **SGR 100020**

Name of Degree: **MASTER OF SCIENCE**

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

SYNTHESIS AND CHARACTERIZATION OF UNSUPPORTED COPPER SULFIDE FOR MERCURY TRAPPING IN AQUEOUS SYSTEM

Field of Study: **MATERIAL SCIENCE**

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work;
- (2) This Work is original;
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature

Date

Subscribed and solemnly declared before,

Witness's Signature

Date

Name: **DR. SHARIFAH BEE ABD HAMID**

Designation: **PROFESSOR**

ABSTRACT

Two phase pure copper sulfides, rhombohedral phase *digenite* (Cu_9S_5) and hexagonal phase *covellite* (CuS) have been successfully prepared via hydrothermal method using copper nitrate and sodium thiosulfate without any assisting agent. The structural, chemical, and thermal properties of the as-synthesized phase pure systems were investigated with various characterization techniques, including powder X-ray diffraction (PXRD), scanning and transmission electron microscopy (SEM and TEM), BET gas sorption, X-ray fluorescence (XRF), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis coupled to mass spectroscopy (TGA-MS), as well as differential scanning calorimetry (DSC) methods. In this study, the phase pure *covellite* has shown a potential ability to remove Hg(II) in aqueous system with maximum sorption capacity of *ca.* 400 mg/ g can be reached at pH 4. The collected experimental data is best fitted to Langmuir isotherm and the sorption of Hg(II) onto *covellite* in aqueous system is favored in a wide range of pH. This was supported by the calculated thermodynamic parameter, ΔG° which has shown that the sorption of Hg(II) onto *covellite* is favorable in a wide range of pH, particularly at low pH. Apart from that, three synthesis parameters (synthesis temperature, Cu: S mole ratio, and synthesis time) have been systematically investigated throughout the study. It was found that synthesis temperature and Cu: S mole ratio determined the phase purity, crystal phase, and morphology of the final products formed; while synthesis time has pronounced effect on the crystallite size of the yields. Furthermore, several mechanistic pathways leading to the final formation of *covellite* were proposed and discussed based on the detailed analysis of PXRD done at different synthesis temperatures. This current study also revealed that the renowned most stable phase in copper sulfide family, *covellite* has transformed into a

mixed phase of pentahydrate copper sulfate and *covellite* at ambient condition after a certain period. It could be shown that *covellite* is an air-sensitive material which undergoes structural changes after exposure to moisture or air. This discovery was supported with various observations from PXRD, EDX, and TG-MS techniques. Therefore, phase stability study was conducted to find out the most efficient way to store copper sulfides besides to investigate the stability of *covellite* over a series of time at ambient condition. The phase stability experiments indicated that *covellite* with the common washing and storage methods described in the research methodology was stable up to 4 weeks. *Covellite* with the purging of nitrogen gas before storage is the best method to prevent *covellite* from further oxidation.

ABSTRAK

Dua fasa tulen kuprum sulfida, iaitu rombohedral *digenite* (Cu_9S_5) dan heksagonal *covellite* (CuS) telah berjaya disediakan melalui kaedah hidroterma dengan menggunakan kuprum nitrat dan natrium thiosulfat tanpa ejen pembantu. Sifat-sifat struktur, kimia, dan terma bagi dua sistem fasa tulen telah dicirikan dengan menggunakan pelbagai kaedah pencirian termasuk kaedah serbuk pembelauan sinar-X (PXRD), mikroskop elektron imbasan dan transmisi (SEM & TEM), penjerapan dan penyahjerapan gas nitrogen (BET), (XRF), taburan tenaga sinar-x (EDX), termagravimetrik-jisim spektroskopi (TGA-MS), dan perbezaan imbasan tenaga (DSC). Dalam kajian ini, fasa tulen *covellite* telah menunjukkan keupayaan untuk menyingkirkan Hg(II) dalam sistem akueus dengan kapasiti penjerapan maksimum yang dicapai ialah kira-kira 400 mg/ g pada pH 4. Data eksperimen yang dikumpul adalah sangat bersesuaian dipadankan dengan isoterma Langmuir dan penjerapan Hg(II) oleh *covellite* adalah cenderung dalam lingkungan pH yang luas di dalam sistem akueus. Perkara ini adalah disokong dengan parameter termodinamik, ΔG° yang menunjukkan penjerapan Hg(II) oleh *covellite* adalah cenderung dalam lingkungan pH yang luas, terutamanya pada pH yang rendah. Selain itu, tiga parameter sintesis (suhu sintesis, nisbah mol Cu: S, dan masa sintesis) telah diselidik dengan bersistematik dalam kajian ini. Suhu sintesis dan nisbah mol Cu: S didapati boleh menentukan fasa tulen, fasa kristal, dan morfologi bagi produk terakhir yang dihasilkan; manakala masa sintesis mempunyai kesan yang ketara dalam saiz kristalit hasil produk. Tambahan pula, beberapa mekanisme yang menunjukkan pembentukan *covellite* telah dicadangkan dan dibincangkan berdasarkan analisis PXRD yang dijalankan secara terperinci pada suhu sintesis yang berbeza. Kajian ini juga menunjukkan bahawa *covellite*, iaitu fasa yang terkenal dengan

kestabilannya dalam keluarga kuprum sulfida, telah tertransformasi kepada fasa campuran kuprum sulfat pentahidrat dan *covellite* pada keadaan ambien selepas suatu jangka masa. Fenomena ini menunjukkan bahawa *covellite* ialah bahan yang sensitif kepada udara dan boleh menjalani perubahan struktur apabila terdedahkan kepada air atau udara. Penemuan ini disokong dengan beberapa perubahan sifat-sifat yang didapati daripada teknik-teknik pencirian seperti PXRD, EDX, dan TG-MS. Oleh sebab itu, kajian fasa kestabilan telah dijalankan untuk mengetahui cara yang sesuai untuk menyimpan kuprum sulfida selain untuk menyelidik kestabilan *covellite* dalam satu siri masa yang tertentu pada keadaan ambien. Ekeperimen fasa kestabilan menunjukkan bahawa *covellite* yang disediakan dengan cara pembasuhan dan penyimpanan yang dihuraikan dalam metodologi penyelidikan ini stabil sehingga 4 minggu. *Covellite* yang disediakan dengan kaedah penyemburan gas nitrogen adalah cara yang terbaik untuk mengelakkan *covellite* daripada proses pengoksidaan yang seterusnya.

ACKNOWLEDGEMENTS

First and foremost, it is my pleasure to thank everyone who has assisted me throughout the journey of completing my master degree. Hereby, I wish to extend my heartfelt gratitude to Prof. Dr. Sharifah Bee Abd Hamid, my supervisor for her advice, assistance, and guidance besides providing me this golden opportunity to involve in this interesting research project. I faithfully wish that the investigation and exploration done on this research topic would lead to a greener, safer, and cleaner dwelling sites which could promote a mercury-free environment to the ecosystems.

My sincere appreciation also goes to Prof. Robert Schlögl, director of Inorganic Chemistry Department, Fritz Haber Institute of the Max Planck Society for his willingness to accommodate my research attachment (about 6 months) in Fritz Haber Institute besides introducing this meaningful project to me. The research experience which I have gained is indeed cultivating my research interest in this respective discipline. I personally very much inspired by his dedication, and determination in pursuing his dreams in research.

I would like to convey my sincere credit to my co-supervisors, Dr. Malte Behrens and Dr. Olaf Timpe for their valuable scientific contributions and useful comments in realizing the truth and facts in science. Not forgotten, great appreciation also goes to Dr. Muralithran Kutty and Dr. Looi Ming Hong for their enthusiasm in sharing their ideas and thoughts.

Besides that, I would like to acknowledge my research partner, Au Yoong Yow Loo for his everlasting support, and useful scientific insights from time to time. I would also like to express my sincere thanks to COMBICAT science officers, all the members of Inorganic Chemistry Department in Fritz Haber Institute, especially those of Nanostructures group for aiding me with sample characterizations as well as technical support besides creating a motivated and enjoyable working environment. I have truly benefited from my research attachment in Berlin.

Furthermore, this research voyage would not have been smoothly sailed without the endurance, encouragement, and moral support from my beloved family and my dear friends. I am grateful for their unconditional love and understanding which have brought me this far.

Last but not least, my special thanks to the financial support from University of Malaya Fellowship Scheme (SBUM) for covering my master studies, Research University Grant, (UMRG: RG022-09AET), and Postgraduate Research Grant (PPP: PS376-2010B) for research funds.

Yap Pei Lay (Emily), 2012.

TABLE OF CONTENTS

	Page
ORIGINAL LITERARY WORK DECLARATION	
ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGMENTS	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES	x
LIST OF TABLES	xiv
LIST OF SYMBOLS AND ABBREVIATIONS	xvi
LIST OF APPENDICES	xix
CHAPTER 1: INTRODUCTION	
1.1 Mercury	1
1.2 Applications of Mercury	8
1.3 Impacts of Mercury	10
1.4 Mercury Remediation	14
1.5 Motivations	21
1.6 Objectives of Research	22
1.7 Outline of Research Work	22
CHAPTER 2: LITERATURE REVIEW	
2.1 Types of Copper Sulfides (Cu_xS)	26
2.2 Applications of Copper Sulfides (Cu_xS)	29
2.3 Historical Development of Hydrothermal Synthesis	31
2.4 Reviews on Copper Sulfides Synthesis Methods	34

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Materials Synthesis	40
3.1.1 Raw Materials	40
3.1.2 Synthesis Equipments	41
3.1.3 Sample Preparation	41
(a) Synthesis of copper sulfides	43
(b) Phase Stability Studies of <i>covellite</i> over Time	46
(c) Application of <i>covellite</i> in Mercury Removal	48
3.2 General Characterization Techniques	49
3.2.1 Structural Analysis	49
(a) Powder X-Ray Diffraction (PXRD)	49
(b) Scanning Electron Microscopy (SEM)	54
(c) Transmission Electron Microscopy (TEM)	57
(d) Nitrogen Adsorption Measurement (BET)	59
3.2.2 Chemical Analysis	65
(a) X-Ray Fluorescence (XRF)	65
(b) Energy Dispersive X-Ray (EDX)	67
3.2.3 Thermal Analysis	70
(a) Thermogravimetric-Mass Spectrometer Analysis (TGA-MS)	70
(b) Differential Scanning Calorimeter (DSC)	74

CHAPTER 4: RESULTS & DISCUSSION

4.1 Effects of Synthesis Temperature	76
4.1.1 Powder X-Ray Diffraction	77
4.1.2 X-ray Fluorescence and Energy Dispersive X-ray Spectrometry	79
4.1.3 Field Emission Scanning Electron Microscopy	82
4.1.4 Discussion	85
4.2 Effects of Cu: S Mole Ratio	91
4.2.1 Powder X-Ray Diffraction	91

4.2.2 X-ray Fluorescence and Energy Dispersive X-ray Spectrometry	95
4.2.3 Field Emission Scanning Electron Microscopy	97
4.2.4 Discussion	100
4.3 Effects of Synthesis Time	104
4.3.1 X-Ray Diffraction	104
4.3.2 X-ray Fluorescence and Energy Dispersive X-ray Spectrometry	106
4.3.3 Field Emission Scanning Electron Microscopy	108
4.3.4 Discussion	111
4.4 Further Studies on Phase Pure Copper Sulfides	113
4.4.1 Properties of Phase Pure Copper Sulfides	113
(a) Elemental Mapping and Atomic Composition	113
(b) Atomic Structure, Morphology and Microstructural Properties	117
(c) Surface Area and Porosity	120
(d) Thermal Stability	123
4.4.2 Application of <i>Covellite</i> in Mercury Removal	134
4.4.3 Discussion	137
4.5 Phase Stability Studies of CuS	139
4.5.1 Evidence of Phase Transformation	140
4.5.2 Phase Stability Studies of CuS over Time	146
4.5.3 Discussion	152
CHAPTER 5: CONCLUSION	
5.1 Concluding Remarks	157
5.2 Recommendations	161
REFERENCES	164
APPENDICES	180

LIST OF FIGURES

		Page
Figure 1.1	Global mercury emissions from natural sources in 2008	7
Figure 1.2	Global mercury emissions from anthropogenic sources in 2008	7
Figure 1.3	Percentages of global mercury demand by use category in 2000 and 2005	10
Figure 1.4	Overview of work scope	23
Figure 3.1	Schematic diagram of overview of research methodology	42
Figure 3.2	Diagram of the typical preparation procedure of Cu _x S powder	44
Figure 3.3	Overview of work procedure for phase stability study over time	47
Figure 3.4	Basic features of a typical PXRD experiment	51
Figure 3.5	Interaction of an electron beam with a thin foil	59
Figure 3.6	Types of physisorption isotherms	61
Figure 3.7	Thermobalance designs in different arrangements	72
Figure 3.8	Schematic diagram of thermogravimetric analysis coupled to mass spectrometry (TGA-MS)	73
Figure 3.9	Diagram of a power compensation DSC	75
Figure 3.10	Diagram of a heat flux DSC	75
Figure 4.1	Temperature vs time profile of hydrothermal reaction measured by thermocouple	77
Figure 4.2	Powder XRD patterns of the as-prepared products at different synthesis temperatures	79
Figure 4.3	XRF analysis of products formed at different synthesis temperatures	81
Figure 4.4	EDX analysis of products formed at different synthesis temperatures	82
Figure 4.5	FESEM micrographs (15 000 × magnification) of products obtained at different synthesis temperatures	83
Figure 4.6	FESEM micrographs (30 000 × magnification) of products obtained at different synthesis temperatures	84

Figure 4.7	FESEM micrographs (60 000 × magnification) of products obtained at different synthesis temperatures	84
Figure 4.8	Overview of proposed mechanism in the formation of CuS	90
Figure 4.9	Colour intensity of reactant mixtures at different Cu: S mole ratio	91
Figure 4.10	Powder XRD patterns of the products obtained with different Cu: S mole ratio	94
Figure 4.11	Crystal compounds formed at different Cu: S mole ratio	94
Figure 4.12	XRF analysis of products formed at different Cu: S mole ratio	96
Figure 4.13	EDX analysis of products formed at different Cu: S mole ratio	97
Figure 4.14	FESEM micrographs (15 000 × magnification) of products obtained with different Cu: S mol ratio	99
Figure 4.15	FESEM micrographs (30 000 × magnification) of products obtained with different Cu: S mol ratio	99
Figure 4.16	FESEM micrographs (60 000 × magnification) of products obtained with different Cu: S mol ratio	100
Figure 4.17	Powder XRD patterns of the products obtained with different synthesis time	104
Figure 4.18	Crystallite size estimation for products synthesized at 3, 6, 8 and 12 hours	106
Figure 4.19	XRF analysis of products formed at different synthesis times	107
Figure 4.20	EDX analysis of products formed at different synthesis times	108
Figure 4.21	FESEM micrographs (15 000 × magnification) of products obtained at different synthesis times	109
Figure 4.22	FESEM micrographs (30 000 × magnification) of products obtained at different synthesis times	110
Figure 4.23	FESEM micrographs (60 000 × magnification) of products obtained at different synthesis times	110
Figure 4.24	FESEM image of product formed at 1 hour	111
Figure 4.25	FESEM image and elemental map of <i>covellite</i>	114
Figure 4.26	FESEM image and atomic composition of <i>covellite</i> at different spots (Area 1)	114

Figure 4.27	FESEM image and atomic composition of <i>covellite</i> at different spots (Area 2)	115
Figure 4.28	FESEM image and elemental map of <i>digenite</i>	116
Figure 4.29	FESEM image and atomic composition of <i>digenite</i> at different spots (Area 1)	116
Figure 4.30	FESEM image and atomic composition of <i>digenite</i> at different spots (Area 2)	117
Figure 4.31	HRTEM images of (a) <i>covellite</i> , CuS in massive material (b) Cross-section of CuS nanoplate (c) Power spectrum shows the lattice fringes from CuS nanoplate	118
Figure 4.32	(a) Electron micrograph of CuS thin platelets under electron beam (beam damage shown in white-dotted line) (b) Beam damage (in white-dotted line) captured on CuS nanoplates (c) Beam damage taking under electron beam (in white-dotted lines); Fourier transform pattern shows d-spacings of monoclinic structure with large unit cell, <i>djurleite</i> (Cu ₃₁ S ₁₆ - PDF 42-564)	118
Figure 4.33	HRTEM images of <i>digenite</i> found in highly agglomerated structure	119
Figure 4.34	Electron micrograph of highly crystalline image captured on <i>digenite</i> sample. Power spectrum of the micrograph illustrates lattice fringes of Cu ₂ S assuming in [102] orientation	120
Figure 4.35	Electron micrograph of highly crystalline image captured on <i>digenite</i> sample. Power spectrum of the micrograph depicts lattice fringes of CuS assuming in [211] orientation	120
Figure 4.36	Nitrogen sorption isotherms of phase pure <i>covellite</i>	122
Figure 4.37	Nitrogen sorption isotherms of phase pure <i>digenite</i>	122
Figure 4.38	Multipoint BET measurement of phase pure <i>covellite</i> sample	123
Figure 4.39	Multipoint BET measurement of phase pure <i>digenite</i> sample	123
Figure 4.40	TG-DSC curve of phase pure CuS (H05) in 100 % Ar gas heated up to 873 K at 5 K/ min with flow rate of 70 cm ³ / min	126
Figure 4.41	TGA-DSC curves of phase pure Cu ₉ S ₅ (H07) in 100 % Ar gas heated up to 873 K at 5 K/ min with flow rate of 70 cm ³ / min	127
Figure 4.42	DTG curve of phase pure Cu ₉ S ₅ (H07) in 100 % Ar gas heated up to 873 K at 5 K/ min with flow rate of 70 cm ³ / min	127

Figure 4.43	Evolution of compounds observed by mass spectroscopy with respect to the mass-to-charge ratio (m/z) for phase pure CuS	128
Figure 4.44	TGA-DSC curve of phase pure CuS (H05) in 21 % O ₂ gas (21 cm ³ /min) and Ar gas (49 cm ³ / min) flow heated up to 873 K at 5 K/min	132
Figure 4.45	TGA-DSC curve of phase pure Cu ₉ S ₅ (H07) in 21 % O ₂ gas (21 cm ³ /min) and Ar gas (49 cm ³ / min) flow heated up to 873 K at 5 K/ min	133
Figure 4.46	DTG curve of phase pure samples in 21 % O ₂ gas (21 cm ³ / min) and Ar gas (49 cm ³ / min) flow heated up to 873 K at 5 K/ min	133
Figure 4.47	Evolution of compounds observed by mass spectroscopy with respect to the mass-to-charge ratio (m/z) for phase pure samples	134
Figure 4.48	Linear plot of <i>Langmuir</i> isotherm at different pH	135
Figure 4.49	PXRD patterns of the (a) single phase CuS and (b) phase transformed CuS	140
Figure 4.50	FESEM images of phase transformed CuS	142
Figure 4.51	EDX analysis on different spots and areas of the phase transformed sample	142
Figure 4.52	TGA-DSC curves of phase transformed CuS in 100 % Ar heated up to 773 K at 5 K/min with flow rate of 100 mL/min	144
Figure 4.53	DTG curve of phase transformed CuS in 100 % Ar heated up to 773 K at 5 K/ min with flow rate of 100 mL/ min	145
Figure 4.54	Evolution of compounds observed by mass spectroscopy with respect to the mass-to-charge ratio (m/z) for phase transformed CuS in 100 % Ar heated up to 773 K at 5 K/ min with flow rate of 100 mL/ min	145
Figure 4.55	PXRD profiles of products dried in furnace after period (a) 1 week (b) 4 weeks (c) 12 weeks	148
Figure 4.56	PXRD profiles of products washed with deionized water and ethanol after period (a) 1 week (b) 4 weeks (c) 12 weeks	149
Figure 4.57	PXRD profiles of products under control study without purging of nitrogen gas after period (a) 1 week (b) 4 weeks (c) 12 weeks	150
Figure 4.58	PXRD profiles of products under control study with purging of nitrogen gas after period (a) 1 week (b) 12 weeks (c) 24 weeks	151

LIST OF TABLES

		Page
Table 1.1	Key properties, transport and fate of different forms of mercury	2
Table 2.1	Classifications of copper sulfides	27
Table 2.2	Types of copper sulfides	28
Table 2.3	Summary on the synthesis of copper sulfides by using different copper source, sulfur source, and assisting agent.	37
Table 3.1	List of chemicals and gas used in the experiments	40
Table 3.2	Instruments and devices involved during Cu_xS preparation and performance testing.	41
Table 3.3	Details of the reactants prepared for synthesis temperature parameter	45
Table 3.4	Details of the reactants prepared for Cu: S mol ratio parameter	45
Table 3.5	Details of the reactants prepared for synthesis time parameter	45
Table 3.6	Details of the samples prepared for phase stability study	47
Table 3.7	Brief summary of PXRD technique	50
Table 3.8	Information content of an idealized diffraction pattern	52
Table 3.9	Brief summary of SEM technique	55
Table 3.10	Brief summary of TEM technique	57
Table 3.11	Brief summary of physisorption measurement	60
Table 3.12	Classification of physisorption isotherms	62
Table 3.13	Brief summary of XRF technique	65
Table 3.14	Brief summary of EDX technique	68
Table 3.15	Factors which influence thermogravimetric measurements	71
Table 4.1	Crystal structures determination by powder XRD for products formed at different temperatures	78
Table 4.2	XRF analysis of samples formed at different temperatures	80
Table 4.3	EDX analysis of samples formed at different temperatures	81
Table 4.4	pH readings of the reaction mixtures at different Cu: S mole ratio	91

Table 4.5	Rietveld quantification analysis for products found with different Cu: S mole ratio	93
Table 4.6	XRF analysis of samples formed at different Cu: S mole ratio	96
Table 4.7	EDX analysis of samples formed at different Cu: S mole ratio	97
Table 4.8	Data distribution of peak profile analysis	105
Table 4.9	XRF analysis of samples formed at different synthesis time	107
Table 4.10	EDX analysis of samples formed at different synthesis time	108
Table 4.11	Results of surface area and porosity for phase pure samples	122
Table 4.12	Transition temperature (T_{onset} & T_{midpoint}), and enthalpy of samples extracted from DSC curve at different heating atmosphere.	124
Table 4.13	Equilibrium data fitted with <i>Langmuir</i> isotherm	135
Table 4.14	Calculated ΔG° at different pH at 25 °C	136
Table 4.15	<i>Rietveld</i> quantification analysis for phase pure and phase transformed products	141
Table 4.16	Transition temperature (T_{onset} & T_{midpoint}), and enthalpy of phase transformed CuS extracted from DSC curve at inert atmosphere	143

LIST OF SYMBOLS AND ABBREVIATIONS

BET	Brunauer-Emmett-Teller
C_2H_5NS	thioacetamide
C_2H_5OH	ethanol
$C_3H_7NO_2S$	L-cysteine
CS_2	carbon bisulfide
CTAB	cetyl trimethyl ammonium bromide
$Cu(ac)_2$	copper (II) acetate
Cu_2S	chalcocite
$Cu_{31}S_{16}$	djurleite
$Cu_{39}S_{28}$	spionkopite
Cu_5FeS_4	bornite
Cu_7S_4	anilite
Cu_8S_5	geerite
Cu_9S_5	digenite
Cu_9S_8	yarrowite
$CuFe_2S_3$	cubanite
$CuFeS_2$	chalcopyrite
CuO	copper oxide
CuS	covellite
CuS_2	villamaninite
$CuSO_4$	copper (II) sulfate
DMDTC	dimethyldithiocarbamate
DSC	Differential Scanning Calorimetry
DTO	dithiooxamide

EDX	Energy Dispersive X-ray Spectroscopy
FeS ₂	pyrite
FESEM	Field Emission Scanning Electron Microscopy
GEb	percentage calculated with reference to global emission
HgS	cinnabar
HRTEM	High Resolution Transmission Electron Microscopy
HSAB	Hard Soft Acid Base
ICP	Inductive Coupled Plasma
K	kelvin
K _{sp}	solubility product constant
LNG	liquefied natural gas
Mg	megagram
MS	Mass Spectroscopy
ng	nanogram
PCP	phenylcyclidine
ppb	parts per billion
Ppk	polyphosphate kinase
ppm	parts per million
PVC	polyvinyl chloride
SAMMS	Self Assembled Monolayers on Mesoporous Silica
SDBS	4-dodecylbenzenesulfonic acid
SDS	sodium dodecyl sulfate
TC	thiocarbonate
Tg	teragram
TGA	Thermogravimetric Analysis

TiO ₂	titanium dioxide
TMR	Total Mercury Removal
TMT	2, 4, 6-trimercaptotriazine
TNT	trinitrotoluene
UNEP	United Nations Environmental Programme
US EPA	United States Environmental Protection Agency
UV	ultraviolet
VCM	vinyl chloride monomer
PXRD	Powder X-ray Diffraction
XRF	X-ray Fluorescence
yr	year

LIST OF APPENDICES

	Page
Appendix A Rietveld refinement analysis for products formed at 25, 35, 65, 95 and 155 °C	180
Appendix B EDX analysis for samples prepared at 25, 35, 65, 95 and 155 °C Example of calculation for XRF & EDX analyses	182
Appendix C Rietveld refinement analysis for products formed at Cu: S mole ratio of 1: 1, 1: 1.5, 1: 2, 1: 2.5, 1: 3, 1: 3.5, 1: 5	186
Appendix D EDX analysis for samples prepared at Cu: S mole ratio of 1: 1, 1: 1.5, 1: 2, 1: 2.5, 1: 3, 1: 3.5, 1: 5	189
Appendix E Peak fitting of characteristic peak of products synthesized at 3, 6, 8 and 12 hours Example of calculation for peak profile analysis	192
Appendix F EDX analysis for samples prepared at 1, 3, 6, and 8 hours	194
Appendix G EDX spectra of phase pure covellite (area 1) prepared at 155 °C, Cu: S mole ratio = 1: 2 for 12 hours	196
Appendix H EDX spectra of phase pure covellite (area 2) prepared at 155 °C, Cu: S mole ratio = 1: 2 for 12 hours	197
Appendix I EDX spectra of phase pure digenite (area 1) prepared at 155 °C, Cu: S mole ratio = 1: 2 for 12 hours	198
Appendix J EDX spectra of phase pure digenite (area 2) prepared at 155 °C, Cu: S mole ratio = 1: 2 for 12 hours	199
Appendix K EDX spectra of phase transformed covellite	200