



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CHARACTERIZATION OF RARE EARTH BARIUM
COPPER OXIDE $[(RE_{1-x}M_x)Ba_2Cu_3O_{7-\delta}]$ VIA COPRECIPITATION
AND ELECTROPHORETIC DEPOSITION METHODS**

MOHD HANIFF BIN WAHID

FS 2010 39

**SYNTHESIS AND CHARACTERIZATION OF RARE EARTH BARIUM
COPPER OXIDE $[(RE_{1-x}M_x)Ba_2Cu_3O_{7-\delta}]$ VIA COPRECIPITATION AND
ELECTROPHORETIC DEPOSITION METHODS**

By

MOHD HANIFF BIN WAHID

MASTER OF SCIENCE

UNIVERSITI PUTRA MALAYSIA

2010



**SYNTHESIS AND CHARACTERIZATION OF RARE EARTH BARIUM
COPPER OXIDE [(RE_{1-x}M_x)Ba₂Cu₃O_{7-δ}] VIA COPRECIPITATION AND
ELECTROPHORETIC DEPOSITION METHODS**

By

MOHD HANIFF BIN WAHID

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirements for the Degree of Master of Science**

November 2010



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

**SYNTHESIS AND CHARACTERIZATION OF RARE EARTH BARIUM
COPPER OXIDE [(RE_{1-x}M_x)Ba₂Cu₃O_{7-δ}] VIA COPRECIPITATION AND
ELECTROPHORETIC DEPOSITION METHODS**

By

MOHD HANIFF BIN WAHID

November 2010

Chairman : Professor Zulkarnain Zainal, PhD

Faculty : Science

Preparation of superconducting material was usually carried out via the solid state reaction technique where oxides and carbonates metal precursors were mixed thoroughly followed by heat treatment. Alternatively, the materials can be prepared via the wet chemistry technique, in which higher homogeneity could be achieved due to initial mixture of cations at atomic scale. In this study, superconductors were prepared via coprecipitation technique from metal acetates which were reacted with oxalic acid as a precipitating agent to form metal oxalates.

Transmission Electron Microscopy (TEM) analysis shows that ultra fine powders of metal oxalates were obtained with the particle size in the range of 9 to 12 nanometers. X-ray diffraction (XRD) analyses confirmed the phases of the metal oxalates. Thermal decomposition and phase formation stages of samples were determined via Thermogravimetric (TG), Differential Thermal Analysis (DTA) and XRD analysis at different heat treatment temperatures.



Minute traces of BaCuO₂ phase was discernible in the X-ray diffraction patterns of sample obtained after sintering at 880 °C for 15 hours. By increasing the sintering temperature up to 970 °C, elimination of the BaCuO₂ phase in YNdBCO samples has succeeded. However, this phase remained in YGdBCO and NdGdBCO samples. Electrical resistivity measurement via 4-point probe technique shows zero resistance temperature, T_{C(R=0)} and T_{C-onset} are (86 K, 95 K), (88 K, 92 K) and (90 K, 98 K) for samples YNdBCO, YGdBCO and NdGdBCO, respectively.

In addition, preparation of superconductor coating were also carried out in this study. Numerous efforts have been reported in fabricating superconductors into certain shapes namely, wires, thin films and many more. The Electrophoretic Deposition (EPD) method is an attractive method where it is low cost, requires simple apparatus, large surface area with uniform thickness of deposits could be obtained and deposits could be designed according to the shape of substrate. In this study, the superconductor coatings were prepared via the EPD method. Several parameters such as colloidal suspension behaviour, voltage of deposition, grinding time, substrate and sintering conditions were investigated in order to obtain good quality coatings.

Colloidal suspension behaviour was investigated via Nanophox particle size analyzer. Smallest particle size distribution was ~ 15 nm by dispersing in acetone. Meanwhile, in order to enhance the deposition of the powders, particle size of the powders need to be reduced. After grinding the powders, deposition was improved and TEM analysis shows that deposited powders are in the range of 30 – 40 nm. To avoid the melting of silver substrates, sintering in argon atmosphere was carried out followed by slow cooling in

oxygen atmosphere. XRD analyses of deposited samples show that orthorhombic 123 phase was obtained YBCO, GdBCO and NdBCO samples however, for YBCO samples the orthorhombicity value was relatively low. Meanwhile, improvement in microstructure was achieved where more dense films were successfully obtained by performing the multi-deposition technique.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENGANALISISAN RARE EARTH BARIUM COPPER OXIDE [(RE_{1-x}M_x)Ba₂Cu₃O_{7-δ}] MENGGUNAKAN KAEDAH PENGENAPAN CAMPURAN DAN PENGENAPAN ELEKTROFORETIK

Oleh

MOHD HANIFF BIN WAHID

November 2010

Pengerusi : Professor Zulkarnain Zainal, PhD

Fakulti : Sains

Penyediaan bahan superkonduktor biasanya dilaksanakan dengan menggunakan kaedah tindak balas struktur pepejal di mana prekursor logam dalam bentuk oksida dan karbonat dicampurkan bersama diikuti dengan pemanasan pada suhu tertentu. Sementara itu, kaedah alternatif untuk penyediaan bahan superkonduktor ini adalah melalui kaedah larutan kimia yang mana kaedah ini menawarkan produk yang lebih homogen disebabkan oleh campuran awal kation pada skala atom. Dalam kajian ini, bahan superkonduktor disediakan melalui kaedah pengenaan campuran di mana prekursor logam yang digunakan adalah logam asetat. Logam ini kemudiannya ditindakbalaskan dengan agen pengenaan iaitu asid oksalik untuk menghasilkan logam oksalat.

Hasil analisis mikroskop elektron transmisi TEM menunjukkan bahawa serbuk halus bersaiz 9 hingga 12 nanometer telah didapati. Manakala, pembelauan sinar X mengesahkan fasa sebatian yang dihasilkan. Penguraian termal dan peringkat



pembentukan fasa telah dikaji menggunakan kaedah termogravimetri TG, DTA dan pembelauan sinar X.

Setelah menjalani pensinteran pada suhu 880 °C selama 15 jam, didapati kewujudan fasa sekunder iaitu BaCuO₂ dalam jumlah yang sedikit terkandung di dalam bahan. Dengan meningkatkan suhu kepada 970 °C fasa sekunder tersebut berjaya dihilangkan dalam sebatian YNdBCO manakala fasa terbabit masih kekal dalam sebatian yang lain. Pengukuran rintangan elektrik melalui kaedah prob-4 menunjukkan nilai $T_{C(R=0)}$ and $T_{C-onset}$ adalah (86 K, 95 K), (88 K, 92 K) dan (90 K, 98 K) bagi sampel YNdBCO, YGdBCO dan NdGdBCO.

Selain daripada itu, penyediaan lapisan superkonduktor juga telah dilaksanakan. Pelbagai usaha telah dijalankan untuk memproses bahan superkonduktor ke dalam bentuk wayar, saput nipis, dan bermacam lagi. Kaedah pegenapan elektroforetik adalah menarik kerana kosnya yang rendah, memerlukan peralatan yang mudah, lapisan dapat memenuhi ruang yang besar serta memiliki ketebalan yang seragam boleh didapati, serta lapisan boleh dihasilkan dalam pelbagai bentuk mengikut bentuk substrat yang digunakan. Dalam kajian ini, lapisan superkonduktor disediakan melalui kaedah pegenapan elektroforetik. Pelbagai pemboleh ubah seperti sifat bahan terampai, voltan yang digunakan untuk pegenapan, masa yang digunakan untuk menghancurkan bahan, bahan substrat yang digunakan dan keadaan pensinteran telah dikaji untuk mendapatkan kualiti lapisan yang terbaik.

Sifat larutan terampai telah dikaji menggunakan alat analisis partikel Nanophox. Serbuk telah didapati tersebar dengan baik dalam aseton berbanding dengan pelarut organik yang lain. Pensinteran bahan telah dijalankan dalam atmosfera argon bagi mengelakkan pencairan substrat. Hasil ujian pembelauan sinar-X ke atas sampel menunjukkan bahawa struktur Kristal ortorombik telah didapati bagi kesemua sampel. Namun, nilai ortorombisiti bagi sampel YBCO adalah agak rendah berbanding dengan nilai yang diperolehi dari JCPDS. Selain daripada itu, kualiti mikrostruktur lapisan telah dapat ditingkatkan di mana lapisan yang lebih padat telah berjaya diperolehi melalui kaedah pegenapan berulang.

ACKNOWLEDGEMENTS

First of all, alhamdulillah, all praise is to Allah where by his Will I managed to accomplish this research work. My special thanks to my supervisory committee members namely, Prof Dr. Zulkarnain Zainal, Prof. Dr. Abdul Halim Shaari, Dr. Tan Kar Ban and Dr. Imad Hamadneh for all the supervision and fruitful discussions which has guided me throughout this research work.

I would also like to express my appreciation to all my colleagues in Lab 2, technical staffs of the faculty and staffs of Microscopy Unit Institute of Bioscience for all the cooperation and support.

Last but not least, my parents, brothers and sisters, my beloved wife and daughter for the unconditional support which forced me to accomplish this research work.



I certify that a Thesis Examination Committee has met on 22nd November 2010 to conduct the final examination of Mohd Haniff bin Wahid on his thesis entitled “Synthesis and Characterization of Rare Earth Barium Copper Oxide [(RE_{1-x}M_x)Ba₂Cu₃O_{7-δ}] via Coprecipitation and Electrophoretic Deposition methods” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Anuar Kassim, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zobir Hussein, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Tan Wee Tee, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Ahmad Kamal Yahya, PhD
Associate Professor
Faculty of Applied Science
Universiti Teknologi MARA
(External Examiner)

SHAMSUDDIN SULAIMAN, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:



This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Zulkarnain Zainal, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Tan Kar Ban, PhD

Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Abdul Halim Shaari, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Imad Hamdneh, PhD

Lecturer
Faculty of Science
University of Jordan
Amman, Jordan

HASANAH MOHD GHAZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:



DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MOHD HANIFF BIN WAHID

Date:



LIST OF TABLES

Table		Page
3.1	Chemical reactions involved in the formation of $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$	35
3.2	Chemical reactions involved in the formation of $Y_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-\delta}$	36
3.3	Chemical reactions involved in the formation of $Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$	37
3.4	Amount of $BaCuO_2$ phase (%) for YGdBCO, YNdBCO and NdGdBCO after sintering	42
3.5	Variation of lattice constants against sintering temperature for YGdBCO, YNdBCO and NdGdBCO	46
3.6	Summarized result of XRF and ICP analysis for YGdBCO, YNdBCO and NdGdBCO sintered at 970 °C / 15 hours	47
3.7	The critical temperature of $REBa_2Cu_3O_{7-\delta}$ (RE : $Y_{0.5}Nd_{0.5}$, $Y_{0.5}Gd_{0.5}$ and $Nd_{0.5}Gd_{0.5}$)	48
3.8	Density of YGdBCO, YNdBCO and NdGdBCO	50
4.1	Lattice constant of YBCO, GdBCO and NdBCO coating determined via least square method	79
4.2	Orthorhombicities of YBCO, GdBCO and NdBCO obtained compared with standard JCPDS files	80



LIST OF FIGURES

Figure		Page
2.1	Cubic perovskite structure. A: Metal cation, B: Smaller metal cation and X: Non-metal anion	6
2.2	Y-123 crystal structure	7
2.3	Graphic illustration of electrophoretic deposition	11
3.1	Flow chart of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE: $\text{Y}_{0.5}\text{Gd}_{0.5}$, $\text{Y}_{0.5}\text{Nd}_{0.5}$, $\text{Nd}_{0.5}\text{Gd}_{0.5}$) metal oxalate precursors synthesis via co-precipitation method	17
3.2	Metal oxalate precursors obtained from co-precipitation	24
3.3	X-ray diffractograms of co-precipitated powders (a) YGdBCO metal oxalate precursor, (b) YNdBCO metal oxalate precursor and (c) NdGdBCO metal oxalate precursor	25
3.4	TEM images of co-precipitated powders at 200,000 x magnification (a) YGdBCO (b) YNdBCO (c) NdGdBCO metal oxalate precursors	28
3.5	TGA thermograms of uncalcined samples. (a) YGd (b) YNd (c) NdGd	31
3.6	DTA thermograms of uncalcined samples. (a) YGd (b) YNd (c) NdGd	31
3.7	XRD patterns of YGd precursor after heating at different temperature	32
3.8	XRD patterns of YNd precursor after heating at different temperature	33
3.9	XRD patterns of NdGd precursor after heating at different temperature	34
3.10	$\text{Y}_{0.5}\text{Gd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared at different sintering temperatures	39
3.11	$\text{Y}_{0.5}\text{Nd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared at different sintering temperatures	40
3.12	$\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared at different sintering temperatures	41
3.13	Plot of BaCuO_2 phase content (%) against sintering temperature	42
3.14	Variation of lattice constants against sintering temperature for sample (a) YGdBCO (b) YNdBCO (c) NdGdBCO	44
3.15	Orthorhombicity of YGdBCO, YNdBCO and NdGdBCO as a function of sintering temperature	46



3.16	Electrical resistance of YGdBCO, YNdBCO and NdGdBCO obtained after sintering at 970 °C / 15 hours in oxygen atmosphere	49
3.17	SEM images of sintered samples at 3000 times magnification (a) YGdBCO, (b) YNdBCO, (c) NdGdBCO	51
4.1	Illustration of coating production via electrophoretic deposition	56
4.2	Schematic of the experimental set up for EPD	58
4.3	X-ray diffractograms of co-precipitated metal oxalate precursors (a) YBCO (b) GdBCO (c) NdBCO	62
4.4	Size of YBCO particles in different organic solvents	63
4.5	Effect of viscosity and relative dielectric constant on size of agglomerates obtained	63
4.6	Photographic images of samples obtained after EPD (a) First attempt of EPD (front view) (b) First attempt of EPD (back view)	64
4.7	Photographic images of samples obtained after EPD (a) Increasing applied voltage (front view) (b) Increasing applied voltage (back view)	65
4.8	(a) EPD coated sample obtained after grinding powders for 1 hour (b) TEM images of deposited powders at 30,000 times magnification	67
4.9	Enlarged TEM image of 4.7 (b)	68
4.10	EPD coated sample treated at 700 °C for 30 minutes (a) Image after heat treatment (b) SEM image of coating's surface at 400 times magnification	69
4.11	Cross-sectional view of coated sample treated at 700 °C for 30 minutes at different magnifications (a) 500x (b) 2500x	70
4.12	Coated sample on titanium (a) As-deposited sample (b) Sintered sample	71
4.13	Samples obtained after sintering in argon atmosphere (a) Sintered at 900 °C / 30 min (b) Microscopic image of green phase observed	72
4.14	Photograph of typical sample obtained after sintering in argon atmosphere (a) and its optical microscope image (b)	73
4.15	XRD of sample sintered at 920 °C / 30 min in argon and its SEM image (b)	74

4.16	SEM images of sample obtained after sintering in argon atmosphere at 920 °C / 30 minutes followed by slow cooling in oxygen at two different magnifications (a) 200x (b) 3000x	75
4.17	Cross sectional view of YBCO sample obtained after sintering in argon atmosphere at 920 °C / 30 minutes followed by slow cooling in oxygen. View under SEM at 250 times magnification	76
4.18	Electrical resistivity measurements of YBCO sintered coating and pure silver substrate as comparison	77
4.19	XRD diffraction patterns of coated YBCO(a) GdBCO(b) and NdBCO (c) by EPD	79
4.20	Electrophoretic coatings of (a) YBCO at 100x magnification (b)GdBCO at 190x magnification (c) NdBCO at 100x magnification	80
4.21	Figure 4.20. YBCO (a), GdBCO(b) and NdBCO(c) coatings at 3000x magnification	82
4.22	Cross sectional image of YBCO coating at different magnifications (a) 700x (b) 3000x	83
4.23	Cross sectional image of GdBCO and NdBCO coatings at different magnifications (a) GdBCO at 140x (b) GdBCO at 3000x (c) NdBCO at 200x (d) NdBCO at 3000x	84

LIST OF APPENDICES

Appendix		Page
A	JCPDS files	
	A1 Yttrium oxalate hydrate (00-033-1460)	101
	A2 Gadolinium oxalate hydrate (00-020-0411)	103
	A3 Neodymium oxalate hydrate (00-020-0764)	106
B	BET analysis	
	B1 YGdBCO oxalate precursor	108
	B2 YNdBCO oxalate precursor	109
	B3 NdGdBCO oxalate precursor	110
C	TG analysis	
	C1 YGdBCO oxalate precursor	111
	C2 YNdBCO oxalate precursor	112
	C3 NdGdBCO oxalate precursor	113
	C4 Weight loss calculation	114
D	Particle size analysis of YBCO powders in different organic solvents	118



LIST OF ABBREVIATIONS

T_C	Critical temperature
YBCO	$YBa_2Cu_3O_{7-\delta}$
RE	Rare earth
J_C	Critical current density
RE-123	$REBa_2Cu_3O_{7-\delta}$
Y-123	$YBa_2Cu_3O_{7-\delta}$
REBCO	$REBa_2Cu_3O_{7-\delta}$
EPD	Electrophoretic deposition
COP	Co-precipitation
XRD	X-ray diffraction
TEM	Transmission Electron Microscope
BET	Brunauer-Emmet-Teller
TG	Thermogravimetric
DTA	Differential Thermal Analysis
XRF	X-ray Fluorescence
ICP	Inductive Coupled Plasma
SEM	Scanning Electron Microscope
JCPDS	Joint Committee on Powder Diffraction Standards
YGdBCO or YGd	$Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$
YNdBCO or YNd	$Y_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-\delta}$
NdGdBCO or NdGd	$Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$
$T_{C(R=0)}$	Critical temperature where resistance is totally zero



$T_{C(\text{onset})}$

Critical temperature where superconducting transition starts



TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	ix
DECLARATION	xi
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF APPENDICES	xvi
LIST OF ABBREVIATIONS	xvii
 CHAPTER	
1	INTRODUCTION 1
1.1	Research problem 1
1.2	Objectives 5
2	LITERATURE REVIEW 6
2.1	Mixing rare earth elements 6
2.2	Electrophoretic deposition 11
3	PREPARATION of REBa₂Cu₃O_{7-δ} (RE:Y_{0.5}Gd_{0.5}, Y_{0.5}Nd_{0.5}, Nd_{0.5}Gd_{0.5}) VIA CO-PRECIPI-TATION TECHNIQUE 15
3.1	Introduction 15
3.2	Experimental 16
3.2.1	Preparation of REBa ₂ Cu ₃ O _{7-δ} (RE:Y _{0.5} Gd _{0.5} , Y _{0.5} Nd _{0.5} , Nd _{0.5} Gd _{0.5}) metal oxalate precursors 16
3.2.2	Characterization of metal oxalate precursors 18



3.2.3	Phase formation study of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE: $\text{Y}_{0.5}\text{Gd}_{0.5}$, $\text{Y}_{0.5}\text{Nd}_{0.5}$, $\text{Nd}_{0.5}\text{Gd}_{0.5}$)	19
3.2.4	Sintering of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE: $\text{Y}_{0.5}\text{Gd}_{0.5}$, $\text{Y}_{0.5}\text{Nd}_{0.5}$, $\text{Nd}_{0.5}\text{Gd}_{0.5}$)	20
3.2.5	Characterization of sintered samples	20
3.3	Results and discussion	23
3.3.1	Co-precipitation of RE-123 (RE: $\text{Y}_{0.5}\text{Gd}_{0.5}$, $\text{Y}_{0.5}\text{Nd}_{0.5}$, $\text{Nd}_{0.5}\text{Gd}_{0.5}$)	23
3.3.2	Physical properties of powders obtained from COP	23
3.3.3	Thermal analysis / Phase formation study	28
3.3.4	Effect of sintering on phase formation	38
3.3.5	Effect of sintering on lattice parameters	43
3.3.6	Elemental analysis	47
3.3.7	Electrical resistivity measurements	48
3.3.8	Density measurements	50
3.3.9	Morphological study	50
3.4	Conclusion	53
4	PREPARATION OF ELECTROPHORETICALLY DEPOSITED $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE:Y, Gd, Nd) COATINGS FROM POWDERS SYNTHESIZED VIA CO-PRECIPIATION TECHNIQUE	55
4.1	Introduction	55
4.2	Experimental	56
4.2.1	Preparation and characterization of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE:Y, Gd, Nd) metal oxalate precursors	57
4.2.2	Particle size analysis by Nanophox particle size analyzer	57
4.2.3	Preparation of YBCO coating via EPD	57

	method	
	4.2.4 Characterization	58
4.3	Results and discussion	60
	4.3.1 Preparation of REBCO (RE : Y, Gd, Nd) powders via co-precipitation technique	60
	4.3.2 Particle size analysis	60
	4.3.3 Preparation of YBCO coatings from calcined powders	64
	4.3.4 Increase voltage	65
	4.3.5 Extending grinding time	66
	4.3.6 Sintering of coated sample	66
	4.3.7 Reduce heat treatment temperature	68
	4.3.8 Replacing silver with titanium	71
	4.3.9 Sintering in argon atmosphere	72
	4.3.10 Sintering in argon atmosphere and increase sintering temperature	73
	4.3.11 Electrical resistivity measurements	76
	4.3.12 Improvement of coating via multi deposition technique	78
4.4	Conclusion	85
5	SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH	87
	REFERENCES	90
	APPENDICES	100
	BIODATA OF STUDENT	120
	LIST OF PUBLICATIONS	120

