

EFFECTS OF Mn SUBSTITUTION IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTING CERAMIC

By

MUSTAFA MUSA ALI DIHOM

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

March 2004

ZOTAC-DDED

This thesis is dedicated to:

My late brother: Khaled

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

EFFECTS OF Mn SUBSTITUTION IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTING CERAMIC

By

MUSTAFA MUSA ALI DIHOM

March 2004

Chairman: Professor Abdul Halim Shaari, Ph. D.

Faculty: Science and Environmental Studies

The influence of manganese (Mn) substitution in copper (Cu), barium (Ba) and yttrium (Y) sites in the Y-Ba-Cu-O system namely: $\text{YBa}_2\text{Cu}_{3-x}\text{Mn}_x\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$), $\text{YBa}_{2-x}\text{Mn}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$) and $\text{Y}_{1-x}\text{Mn}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$) were studied. The samples were prepared using the conventional solid state sintering technique. The sintered temperature and soaking time were 920°C and 24 hours respectively. The transport properties of the samples were measured using the four-point probe electrical resistance measurement and the magnetic properties were measured by using ac susceptibility. Scanning electron microscope (SEM) was used to identify the surface morphology while the phase of the samples was determined using x-ray diffraction (XRD) technique.

The pure sample, which exhibits $T_{C(R=0)}$ around 90 K and $T_{C\text{onset}}$ around 94 K showed large flaky grains of $\sim 25 \mu\text{m}$ in size with some gaps and voids. The effect of Mn substitution on the superconducting behaviour of YBCO shows that the transition

temperature, T_C was sharply reduced when the substitution site is at Ba. For the sample in which $x=0.30$ the values of T_C are 80K, 72K and 60K for substitution in the Y, Cu and Ba sites, respectively.

The dynamic magnetic properties of the samples show that the effect of Mn substitution is markedly decreased in the Ba substituted samples. The value of Josephson current I_0 for $x=0.3$ are 13.6 μ A, 14.1 μ A and 6.9 μ A for the substitution in Y, Ba and Cu sites, respectively. The XRD patterns showed that the orthorhombic structure was retained for all the samples. However, at higher concentration of Mn substitution, some unknown peaks were observed. There is a general trend of an increase of (102) peaks as Mn concentration increases at all sites, while the (003) and (006) peaks decreased.

The morphology of the samples varies as Mn was substituted at different sites. At lower concentration, the shapes of the grains are sharper in Mn substituted the Y samples. When $x=0.3$, the grains are loosely packed and more rounded when Mn substituted the Ba sites. When manganese was incorporated in Y^{3+} , Ba^{2+} and Cu^{2+} sites, the resistivity result showed the shifting in $T_{C(R=0)}$ towards low temperature as the Mn increases.

The temperature dependence of ac susceptibility data χ' shows the shifting of the onset diamagnetism towards lower temperature as the Mn concentration increased

due to the presence of low T_C phase. The imaginary component, χ'' shows a decrease in the intergranular coupling peak, T_p towards lower temperature as the Mn concentration increased. XRD patterns showed the existence of the unknown peaks, which belong to the impurities. SEM micrographs showed the decrease in the grain size as the concentration increases.

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

**KESAN PENGGANTIAN Mn DALAM BAHAN SERAMIK
SUPERKONDUKTOR $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$**

Oleh

MUSTAFA MUSA ALI DIHOM

Mac 2004

Pengerusi: Profesor Abdul Halim Shaari, Ph. D

Fakulti: Sain dan Pengajian Alam Sekitar

Pengaruh penggantian mangan (Mn) ke dalam kuprum (Cu), barium (Ba) dan yitrium dalam sistem Y-Ba-Cu-O, iaitu $\text{YBa}_2\text{Cu}_{3-x}\text{Mn}_x\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$), $\text{YBa}_{2-x}\text{Mn}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$) dan $\text{Y}_{1-x}\text{Mn}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0.00 \geq x \geq 0.5$) telah dikaji. Sampel-sampel disediakan dengan menggunakan teknik lazim keadaan pepejal. Suhu sinter dan masa meresap adalah masing-masing 920°C dan 24 jam. Ciri-ciri pengangkutan bagi sampel telah diukur dengan menggunakan pengukuran rintangan elektrik 4 titik dan ciri-ciri magnetik telah diukur dengan menggunakan kaedah kerentanan au. Mikroskop pengimbas elektron (SEM) telah digunakan untuk mengenalpasti permukaan morfologi sementara fasa bagi sampel telah ditentukan menggunakan teknik belauan sinar-x (XRD).

Sampel tulen mempamerkan $T_{c(R=0)}$ dalam 90K dan $T_{c \text{ mula}}$ dalam 94K menunjukkan saiz butiran besar lebih kurang $25\mu\text{m}$ dengan sedikit liang.

Penggantian Mn terhadap YBCO menunjukkan suhu peralihan T_c mengurang dengan mendadak apabila penggantian di tapak Ba dilakukan. Untuk sampel di mana $x=0.3$,

nilai T_c adalah 80K, 72K dan 60K untuk penggantian dalam bahagian Y, Cu dan Ba masing-masing.

Ciri-ciri magnetik yang dinamik bagi semua sampel menunjukkan bahawa penggantian mangan (Mn) menyebabkan T_c menurun secara mendadak dengan penggantian Ba. Nilai arus Josephson, I_0 pada $x=0.3$ adalah $13.6\mu A$, $14.0\mu A$ dan $6.9\mu A$ untuk

penggantian dalam Y, Ba dan Cu masing-masing

Bentuk corak pembelauan sinar-X menunjukkan struktur ortorombik telah diperolehi untuk semua sampel. Walau bagaimanapun, bagi peningkatan Mn yang berkepekatan tinggi, beberapa puncak tidak dikenali dapat dilihat. Terdapat arah peningkatan umum puncak-puncak (102) seperti peningkatan kepekatan Mn pada setiap sudut, sementara puncak (003) dan (006) berkurangan.

Morfologi sampel berbeza sebagaimana penggantian Mn pada kekisi yang berlainan. Bentuk butiran lebih tajam di dalam sampel dimana Mn menggantikan Y pada kepekatan yang rendah. Apabila $x=0.3$, butiran adalah longgar dan lebih bulat bagi penggantian Mn kepada kekisi Ba.

Apabila mangan di masukkan ke dalam tapak Y^{3+} , Ba^{2+} and Cu^{2+} , keputusan kerintangan menunjukkan peralihan $T_{C(R=0)}$ kepada suhu rendah dengan pertambahan Mn. Pergantungan data kerentanan ac χ' menunjukkan peralihan diamagnet mula kepada suhu rendah dengan pertambahan kepekatan Mn disebabkan kehadiran fasa T_C rendah. Komponen khayalan, χ'' menunjukkan pengurangan dalam puncak gandingan antara butir, T_p kepada suhu rendah dengan petambahan kepekatan Mn. Corak XRD

menunjukkan kewujudan puncak-puncak tidak dikenali, yang dipunyai oleh bendasing. Mikrograf SEM menunjukkan pengurangan saiz butir dengan pertambahan kepekatan.

ACKNOWLEDGEMENTS

In the name of Allah, the most Gracious and the most Merciful, all praised be to Allah the Almighty, for giving me the strength and health to write and lastly completed this thesis.

I am extremely grateful to my supervisor, Professor Dr. Abdul Halim Shaari for the patience, guidance, advice, ideas, critics, encouragement and continuous support. My deepest gratitude also goes to my co-supervisor, Professor Dr. W.M Mat.Yunus and Dr. A.W. Zaidan for their comments, suggestions and wise guidance throughout the research work.

I am indebted to the kind assistance and guidance from my previous lab mate Dr. Imad Hamadneh. Further thanks with appreciation goes to my lab mates, in particular Kabashi, Ali, Ramadan, Zohra, Iftetan, Azman and Abdullah Chik, for their kind help and understanding in this work. Also, I would like to take this opportunity to thank the members and staff in the Physics Department for providing an environment and platform to conduct this study.

Lastly but not least, I thank my parents, brothers, sisters, and my wife for their understanding, support and encouragement, who gave me the encouragement to complete this work.

I certify that an Examination Committee met on 9th March 2004 to conduct the final examination of Mustafa Musa Ali Dihom on his Master of Science thesis entitled “Effects Of Mn Substitution In $YBa_2Cu_3O_{7-\delta}$ Superconducting Ceramic” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Sidek Ab Aziz, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mansor Hashim, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Noorhana Yahya, Ph.D.

Lecturer
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Roslan Abd. Shukor, Ph.D

Professor
Faculty of Science
Universiti Kebangsaan Malaysia
(Independent Examiner)

GULAM RUSUL RAHMAT ALI,
Ph.D. Professor/Deputy Dean
School of Graduate Studies,
Universiti Putra Malaysia

Date:

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

Abdul Halim Shaari, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

W. Mahmood Mat Yunus, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Zaidan Abdul Wahab, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.

Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Mustafa Musa Ali Dihom

Date:

TABLE OF CONTENTS

	<i>Page</i>	
DEDICATION	ii	
ABSTRACT	iii	
ABSTRAK	vi	
ACKNOWLEDGEMENTS	ix	
APPROVAL	x	
DECLARATION	xii	
LIST OF TABLES	xv	
LIST OF PLATES	xvi	
LIST OF FIGURES	xviii	
LIST OF SYMBOLS AND ABBREVIATIONS	xxiii	
		CHAPTER
I	INTRODUCTION	1
	Basic phenomena of the superconductivity	1
	Type I superconductor	3
	Type II superconductor	3
	High temperature oxide superconductor	5
	Y-Ba-Cu-O system	6
	Favourable properties of YBCO	9
	History of superconductors	9
	Objective of the Research	11
II	LITERATURE REVIEW	12
	Effect of Doping	12
	Copper Doping	12
	Barium Doping	18
	Yttrium Doping	19
III	THEORIES ABOUT SUPERCONDUCTORS	26
	BCS Theory	26
	Cooper Pairs	26
	Bandgap	27
	Energy Gap	28
	London Brother's Theory	28
	Ginzburg-Landau Theory	29
	Abrikosov's Theory	30
	Theory of AC Susceptibility	31
IV	METHODOLOGY	33
	Introduction	33
	Sample preparation	33
	Preparation of starting chemicals	33
	Calcination	34
	Final Sintering	34

	Standard Characterization of YBCO Superconductors	37
	X-ray Diffraction (XRD)	37
	Electrical Resistance Measurement	39
	AC Susceptibility Measurement	40
	Microstructure Analysis	45
V	RESULTS AND DISCUSSION	46
	Resistance Measurement	46
	Effect of Mn doping in Cu site of Y-Ba-Cu-O samples	46
	Effect of Mn doping in Ba site of Y-Ba-Cu-O samples	48
	Effect of Mn doping in Y site of Y-Ba-Cu-O samples	51
	AC Susceptibility Measurements	53
	Effect of Mn in Cu site	56
	Effect of Mn in Ba site	68
	Effect of Mn in Y sites	78
	X-ray Diffraction Analysis	89
	Effect of Mn in Cu site	89
	Effect of Mn in Ba site	93
	Effect of Mn in Y site	96
	Microstructure Analysis	101
	Effect of Mn in Cu site	101
	Effect of Mn in Ba site	107
	Effect of Mn in Y site	113
VI	CONCLUSIONS AND SUGGESTIONS	119
	Conclusions	119
	Suggestions	121
	BIBLIOGRAPHY	122
	APPENDICES	127
	BIODATA OF THE AUTHOR	129