UNIVERSITI PUTRA MALAYSIA

STRUCTURE, MICROSTRUCTURE AND SUPERCONDUCTIVITY OF YBa2Cu3O7- WITH MAGNETIC NANOPARTICLE ADDITIVES

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FS 2010 6

STRUCTURE, MICROSTRUCTURE AND SUPERCONDUCTIVITY OF $YBa_2Cu_3O_{7-\delta}$ WITH MAGNETIC NANOPARTICLE ADDITIVES

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MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2010

STRUCTURE, MICROSTRUCTURE AND SUPERCONDUCTIVITY OF $YBa_2Cu_3O_{7-\delta}$ WITH MAGNETIC NANOPARTICLE ADDITIVES

By

MOHD KAMARULZAMAN BIN MANSOR

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

February 2010

DEDICATION

To my mom and dad who love me so much

MALINI BINTI HUSSIN
MANSOR BIN AHMAD

Beloved wife

HASNIDAR BINTI HAMID

Son

MUHAMMAD FATHI BIN MOHD KAMARULZAMAN

Sisters

NORSURIANI BINTI MANSOR
NORHAFIZZAH BINTI MANSOR

Nephews

AMIR HARITH IMTIYAZ
AFEEF HAZMAN IMTIYAZ

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

STRUCTURE, MICROSTRUCTURE AND SUPERCONDUCTIVITY OF $YBa_2Cu_3O_{7-\delta}$ WITH MAGNETIC NANOPARTICLE ADDITIVES

By

MOHD KAMARULZAMAN BIN MANSOR

February 2010

Chairman: Professor Abdul Halim Shaari, PhD

Faculty: Science

Potential enhancement of flux pinning by rare-earth (RE) magnetic nanoparticles added into bulk of $YBa_2Cu_3O_{7-\delta}$ (YBCO) was studied experimentally. In particular, a comprehensive investigation of crystal structure, microstructure and superconducting properties of YBCO added with *x* weight percent (x = 0.0 - 0.6 wt. %) of nanosized (≤ 25 nm) Nd_2O_3, Sm_2O_3, Gd_2O_3 and Yb_2O_3 prepared via solid state technique was presented. X-ray diffraction (XRD) technique was used for crystal structure and phase formation identification. Detailed crystal structure analysis was carried out on each sample using the Rietveld refinement technique. The fractured cross section microstructure was observed using Scanning Electron Microscopy (SEM) and support by elemental analysis using Energy Dispersive X-ray (EDX) spectroscopy. Four point probe technique were employed to study the resistance dependence from room temperature down to 50 K.

The XRD patterns revealed that only YBCO phase peaks were observed for sample with $x \leq 0.3$ and minor intensities of 211 secondary phase was observed for $x \geq 0.4$ in each

series. The XRD patterns of all samples were indexed in the orthorhombic structure with space group *Pmmm.* All refined R_{wp} factor values are in between 9 % - 12 % different, which support the refined structure model reasonably and reflected that the refined curve fit well with the measured ones. Refinement of the XRD patterns indicated that magnetic nanoparticles added changed the lattice constants of the unit cell due to the rare-earth (RE) ionic radius and their replacement sites. RE^{3+} was found to incorporate into the crystal structure and could replace either the Y-site or Ba-site. The size of the lattice mismatch created between non-substituted and substituted unit cell was comparable to the size of the vortex core which may provide a potential flux pinning sites.

Surface microstructure study showed the grain size, grain boundary and porosity of the each series was significantly influenced by the concentration of additives. Grain size in each series become smaller from low to high concentration and the mixture between rectangular plate-like and granular grains was observed. The change in microstructure significantly influenced the absolute value of resistance in the normal state. EDX analysis showed a typical YBCO energy spectrum together with added element in the samples. The energy spectrum corresponding to the added elements become more prominent as x increased confirming that RE^{3+} was actually incorporated into the system.

The metallic behavior in the normal state of samples added with Gd_2O_3 and Yb_2O_3 was maintained until higher value of x added. However, the normal state behavior changes from metallic to semiconducting when the concentration of Nd_2O_3 and Sm_2O_3 increased. With the increase of additive concentration, the superconducting transition temperature decreased from 92 K to a lower value depending on the type of additives and the weight percent added. The depression of $T_{c\text{-}zero}$ value has been attributed by the variation of the mobile carrier density in the CuO_2 plane and various structure changes. It may also be due to the Cooper pair breaking caused by the RE^{3+} which partially substituted at Y-site and Ba-site in crystal structure.

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

STRUKTUR, MIKROSTRUKTUR DAN KESUPERKONDUKSIAN $YBa_2Cu_3O_{7-\delta}$ DENGAN ADITIF ZARAH NANO BERMAGNET

Oleh

MOHD KAMARULZAMAN BIN MANSOR

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Potensi peningkatan pusat pengepinan fluks oleh bahan magnet nadir bumi berzarah nano ditambah dalam $YBa_2Cu_3O_{7-\delta}$ (YBCO) telah dikaji secara ekperimen. Secara khusus, penyelidikan secara meluas terhadap struktur kristal, mikrostruktur dan sifat superkonductor YBCO pukal ditambah dengan *x* peratus berat (x = 0.0 - 0.6 peratus berat) Nd_2O_3, Sm_2O_3, Gd_2O_3 dan Yb_2O_3 bersaiz nano (≤ 25 nm) yang disediakan melalui teknik keadaan pepejal telah ditunjukkan. Teknik pembelauan sinar-X telah digunakkan untuk mengenalpasti struktur hablur dan juga fasa yang terbentuk. Analisis secara mendalam telah dijalankan terhadap semua sampel dengan mengunakan teknik pemurnian Rietveld. Mikrostruktur patahan keratan rentas telah dilihat dengan menggunakan Mikroskop Pengimbas Elektron dan disokong oleh analisis unsur dengan menggunakan spektroskopi Penyerakan Tenaga Sinar-X. Penduga empat titik digunakan untuk mengkaji perubahan rintangan terhadap suhu dari suhu bilik kepada 50 K.

Corak pembelauan sinar-X menunjukkan fasa tunggal YBCO bagi sampel dengan $x \leq 0.3$ dan fasa sekunder 211 minor dapat dilihat bagi $x \geq 0.4$ bagi setiap siri. Corak pembelauan sinar-X dapat diindekskan dalam struktur ortorombik dengan kumpulan ruang *Pmmm*. Semua nilai faktor R_{wp} adalah antara 9 % - 12 %, yang menyokong model struktur permunian secara munasabah dan membayangkan bahawa lengkungan termurni adalah sepadan dengan yang telah dikira. Pemurnian corak pembelauan sinar-X menunjukkan bahawa nano zarah yang ditambah telah mengubah pemalar kekisi dalam sel unit bergantung terhadap jajari ion RE^{3+} dan tapak penggantian. RE^{3+} di dapati masuk ke dalam struktur hablur dan boleh mengantikan sama ada tapak-Y atau tapak-Ba. Saiz ketidak sepadanan yang terbentuk antara sel unit yang terganti dan tidak terganti adalah sebanding dengan teras pusar dan ianya menyediakan tapak yang berpotensi sebagai pusat pengepinan fluks.

Kajian mikrostruktur permukaan menunjukkan bahawa saiz butiran, sempadan antara butiran dan keadaan berliang dalam setiap siri terpengaruh oleh jumlah aditif. Saiz butiran dalam setiap siri menjadi semakin kecil daripada jumlah aditif yang rendah kepada jumlah aditif yang tinggi dan campuran antara kepingan seperti segi empat tepat dan butiran dapat diperhatikan. Perubahan dalam mikrostruktur telah mempengaruhi nilai sebenar rintangan pada keadaan normal. Analysia Penyerakan Tenaga Sinar-X menunjukkan spektrum tenaga yang lazim bagi YBCO bersama unsur aditif dalam setiap sampel. Spektrum tenaga yang sepadan dengan unsur aditif menjadi lebih menonjol apabila nilai *x* meningkat dan mengesahkan bahawa RE^{3+} sebenarnya masuk ke dalam sistem hablur.

Sifat metalik pada keadaan normal bagi sampel yang ditambah dengan Gd_2O_3 dan Yb_2O_3 adalah kekal sehingga nilai tertinggi. Walau bagaimanpun sifat pada keadaan normal berubah daripada sifat metalik kepada semikonduksian apabila jumlah Nd_2O_3 dan Sm_2O_3 meningkat. Dengan penambahan jumlah bahan aditif, nilai suhu peralihan berkurangan daripada 92 K kepada nilai yang lebih rendah berkantung kepada jenis aditif dan peratus berat yang ditambah. Penurunan pada nilai $T_{c\text{-}zero}$ adalah disebabkan oleh perubahan kepadatan mobil pembawa dalam satah CuO_2 dan kepelbagaian perubahan struktur. Ianya juga mungkin disebabkan oleh pemisahan pasangan Cooper oleh RE^{3+} yang telah terganti secara separa pada tapak-Y dan tapak-Ba dalam struktur hablur.

ACKNOWLEDGEMENTS

First and foremost, I would like to extent my deepest praise to Allah s.w.t that has given me patience, strength, determination and courage to complete this research. I would like to express my utmost gratitude to Prof. Dr. Abdul Halim Shaari, Dr. Cheen Soo Kien and Dr. Malik Idries Adam for their constant monitoring, support, encouragement and sponsoring during period of this research. Working with them has provided me with vast understanding on materials science and theoretical knowledge from which I will continue to draw benefit in the future.

I am grateful to my group members Mohd Faisal Mohd Aris, Dr. Walter Charles Primus, Dr. Kong Wei and all my laboratory colleague for their tremendous assistance and support throughout this study. I am also grateful to Madam Yasmin and Mr. Rafi from SEM unit in Institute Biosains (IBS) for their guidance and assistance.

Finally, I would like to express my fullest appreciation to my parents for being so understanding. To my mom and my wife, I love both of you so much.

M. Kamarulzaman

I certify that a Thesis Examination Committee has met on 23 February 2010 to conduct the final examination of Mohd. Kamarulzaman Bin Mansor on his thesis entitled "Structure, Microstructure and Superconductivity of $YBa_2Cu_3O_{7-\delta}$ with Magnetic Nanoparticle Additives" 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 degree of Master.

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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. The members of the Supervisory Committee were as follows:

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Date: 13 May 2010

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 KAMARULZAMAN BIN MANSOR

Date: 23 February 2010

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LIST OF ABBREVIATIONS

YBCO	Yttrium Barium Copper Oxide
YbBCO	Ytterbium Barium Copper Oxide
NdBCO	Neodymium Barium Copper Oxide
Y123	Yttrium Barium Copper Oxide
Pr123	Praseodymium Barium Copper Oxide
REBCO	Rear-earth Barium Cooper Oxide
HTSC	High Temperature Superconductor
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersion X-ray
TEM	Transmission Electron Microscopy
ZFC	Zero Field Cool
UPM	Universiti Putra Malaysia
PLD	Pulse Laser Deposition
DC	Direct Current
RE	Rare-earth
U.S	United State
1 G	First generation
2 G	Second generation
A	Ampere
I	Current
R	Resistance

V	Voltage
X	Magnification
N	Total number of points
P	Adjusted parameters
C	Number of constrains applied
B	Magnetic Field
H	Magnetic Field
H_e	Magnetic field applied
H_c	Critical field
M	Magnetization
H_{c2}	Upper critical magnetic field
H_{c1}	Lower critical magnetic field
T_c	Critical temperature
J_c	Critical current
T_s	Spin gap temperature
$T_{c\text{-Onset}}$	Onset critical temperature
$T_{c\text{-zero}}$	Zero critical temperature
$T_{c\ max}$	Maximum critical temperature
ΔT_c	Delta critical temperature
wt.	Weight
nm	Nanometer
mm	Millimeter
µm	Micrometer

kV	Kilovolt
R_{exp}	Expected R-factor
R_{wp}	Weighted pattern R-factor
R_p	Profile R-factor
Y_{oi}	Observed intensities
Y_{ci}	calculated intensities
Σ_i	Total of steps
i	Number of step
W_i	Weight
a	Lattice parameter
b	Lattice parameter
c	Lattice parameter
V	Unit cell volume
p	Hole concentration
x	Amount of weight percent added
θ	Theta
ξ	Coherence length
δ	Delta
$=$	Equal
$\leq$	Less than or equal to
$\geq$	Greater than or equal to
$>$	Bigger than
Å	Angstrom Unit