UNIVERSITI PUTRA MALAYSIA

EFFECT OF NANOPARTICULATES (Gd_2O_3, Eu_2O_3, Ce_2O_3) ADDITION ON PROPERTIES OF $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10}$ CERAMICS SUPERCONDUCTORS

SAEEDEH SADAT HOSSEINI RAVANDI

FS 2009 13

EFFECT OF NANOPARTICULATES (Gd_2O_3, Eu_2O_3, Ce_2O_3) ADDITION ON PROPERTIES OF $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10}$ CERAMICS SUPERCONDUCTORS

By

SAEEDEH SADAT HOSSEINI RAVANDI

Thesis submitted to the senate of University Putra Malaysia in fulfillment of the requirements for the degree of Master of Science

May 2009

DEDICATIONS

To Prof. Dr. Halim,

for his guidance, patience and belief in me…

To my parents, Javad, Mahrokh and my lovely Mohammad,

for their love, support and understanding…

Abstract of thesis presented to the senate of University Putra Malaysia in fulfillment of requirements for the degree of Master of Science.

EFFECT OF NANOPARTICULATES (Gd_2O_3, Eu_2O_3, Ce_2O_3) ADDITION ON PROPERTIES OF ($Bi_{1.6}Pb_{0.4}$)$Sr_2Ca_2Cu_3O_{10}$ CERAMICS SUPERCONDUCTORS

By

SAEEDEH SADAT HOSSEINI RAVANDI

May 2009

Chairman : Professor Abdul Halim bin Shaari

Faculty : Science

The effects of Rare Earth oxide (M) nanoparticulates addition in $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10} + xM$ with M = Gd_2O_3, Eu_2O_3, Ce_2O_3 and x = 0.0-0.05 system, prepared by the conventional solid state reaction method have been investigated for structural, electrical and magnetic properties. The sizes of nanoparticulates oxide are 150 nm, 4 nm and 50nm respectively for Gd_2O_3, Eu_2O_3 and Ce_2O_3. The samples were calcined at 800° C and 830° C for 48 hours followed by sintering at 850° C for 120 hours. The morphological appearance of the samples with Gd_2O_3 addition generally showed platelet-like grains with random orientations, typically of 2223 phase's structure, and by increasing the amount of nanoparticulate the platelet tend to stick together. At high percentage of nanoparticulate addition in Gd_2O_3 the microstructure displayed grain size from to 1.5 μm to 10 μm and increased

number of pores. The morphologies of fractured surface of pellets of specimen from x=0.00-x=0.05 Ce_2O_3 nanoparticulate, showed that the flaky nature of the grains gradually vanished and the edges of the grains become softer and the size of the grain changed from 10 µm to 2 µm. At x=0.03 of Eu_2O_3 the grain size become larger in comparison with other samples.

The volume fraction of the high-T_C (2223) phase for addition of Gd_2O_3 decreased from 89% for x=0.005 to 58% for x=0.05 and in the low- T_C (2212) phase the volume increased from 3.4% to 41.2 % for x=0.005 and x=0.05, respectively. The c-axis parameter decreased from 37.1293 Å to 36.7800 Å at x=0.005 to x=0.05 for Gd_2O_3 addition on Bi-2223. For addition with Eu_2O_3, we can observe some increasing in x=0.03, from x=0.01-x=0.03 volume fractions increased from x=0.01-x=0.03 according to following percentage of 83.2% to 94.3%, respectively. The lattice parameter in the c-axis increased for x=0.00 to x=0.03 in Eu_2O_3 addition from 37.1264 Å to 37.1432 Å. In addition with Ce_2O_3 nanoparticulate in pure Bi-2223, with increasing in the amount, the volume fractions reduced from 92.67% for x=0.00 to 57% in x=0.05, the c-axis also decreased from 37.1193Å to 36.8870Å for x=0.00-0.05.

The critical temperature with increasing amounts of Gd_2O_3 x=0.00-x=0.05 decreased from 101 K to 96 K, respectively. For samples with the addition of Eu_2O_3, T_C decreased from 101 K to 98 K and started to increase for x=0.03 with T_C =103.74 K. When Ce_2O_3 content was further increased, the electrical behavior started to change. The onset critical temperatures were reduced from 101 K to 93 K for x=0.00-x=0.05, respectively. Measurements of AC magnetic susceptibility as a function of temperature and AC field amplitudes have been carried out for samples containing Gd_2O_3 nanoparticulate at constant frequency f=333.3 Hz. It is shown that with increasing addition content from x=0.00- x=0.05, the diamagnetic onset temperature decreased from 107 K for pure sample to 97 K for Gd_2O_3 in last content. The analysis for comparison is based on the availability of higher percentage of the high-T_C (2223) phase in the sample, the suppression degree of diamagnetic behavior with respect to AC fields; rapid or slow shift of the summit in $\chi''_{(T)}$ to lower temperature with increasing field amplitude and the sharpness of $\chi'_{(T)}$ for the intergranular component for the same field amplitude.

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

KESAN PENAMBAHAN NANOZARAH (Gd_2O_3, Eu_2O_3, Ce_2O_3) KE ATAS SIFAT-SIFAT SUPERKONDUKTOR SERAMIK $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10}$

Oleh

SAEEDEH SADAT HOSSEINI RAVANDI

Mei 2009

Pengerusi: **Professor Abdul Halim bin Shaari**

Fakulti: **Sains**

Kesan penambahan nanozarah oksida nadir bumi (M) ke dalam sistem $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10} + x$M dengan M = Gd_2O_3, Eu_2O_3, Ce_2O_3 dan x = 0.0-0.05, yang disediakan dengan kaedah tindakbalas keadaan pepejal yang konvensional telah dikaji struktur, sifat elektrik dan sifat magnetnya. Saiz oksida nanozarah adalah masing-masing 150 nm, 4 nm dan 50 nm untuk Gd_2O_3, Eu_2O_3 dan Ce_2O_3. Sampel-sampel telah dikalsin pada 800° C dan 830° C selama 48 jam diikuti dengan persinteran pada suhu 850° C selama 120 jam. Rupa bentuk morfologi sampel-sampel dengan penambahan Gd_2O_3 secara amnya menunjukkan butiran-butiran seperti platlet dengan orientasi yang rawak, khasnya untuk struktur fasa 2223, dan dengan menambahkan amaun nanozarah platlet tersebut cenderung untuk melekat bersama. Pada peratusan penambahan nanozarah Gd_2O_3 yang tinggi mikrostruktur menunjukkan saiz butiran dari 10 μm kepada

1.5 μm dan peningkatan bilangan keliangan. Morfologi permukaan retakan pelet bagi spesimen dengan nanozarah Ce_2O_3 dari $x = 0.00 - x = 0.05$, menunjukkan bahawa keadaan kelupasan pada butiran hilang secara beransur-ansur dan bahagian sisi butiran menjadi semakin licin dan saiz butiran berubah dari 10 μm kepada 2 μm. Bagi Eu_2O_3 pada $x = 0.03$ saiz butiran menjadi lebih besar berbanding dengan sampel-sampel lain.

Pecahan isipadu bagi fasa T_C-tinggi (2223) bagi penambahan Gd_2O_3 berkurang dari 89 % untuk $x = 0.005$ kepada 58 % untuk $x = 0.05$ dan dalam fasa T_C-rendah (2212) isipadu meningkat dari 3.4 % kepada 41.2 % bagi $x = 0.005$, $x = 0.05$, masing-masing. Pemalar paksi-*c* berkurang dari 37.1293 Å kepada 36.7800 Å pada $x = 0.005$, $x = 0.05$ bagi penambahan Gd_2O_3 ke atas Bi-2223. Untuk penambahan dengan Eu_2O_3, dapat diperhatikan sejumlah peningkatan dalam $x = 0.03$, dari $x = 0.00$ kepada $x = 0.03$ pecahan isipadu meningkat menurut peratusan berikut iaitu 83.2 % kepada 94.3 %, masing-masing. Pemalar kekisi dalam paksi-*c* meningkat dengan penambahan Eu_2O_3 $x = 0.00$ kepada $x = 0.03$ dari 37.1264 Å kepada 37.1432 Å. Bagi penambahan dengan nanozarah Ce_2O_3 ke dalam Bi-2223 tulen, dengan penambahan amaunnya, pecahan isipadu berkurang dari 92.6 7% bagi $x = 0.00$ kepada 57 % bagi $x = 0.05$, paksi-*c* juga berkurang dari 37.1193Å kepada 36.8870Å bagi $x = 0.00$-0.05. Suhu genting dengan penambahan amaun Gd_2O_3 $x = 0.00 - x = 0.05$ berkurang dari 101 K kepada 96 K, masing-masing. Dengan penambahan Eu_2O_3 T_C berkurang dari 101 K kepada 98 K dan mula meningkat bagi $x = 0.03$ dengan T_C =103.74 °K. Apabila kandungan Ce_2O_3 terus ditingkatkan, sifat elektrik akan mula berubah. Suhu genting permulaan berkurang dari 101 K to 93 K bagi $x = 0.00 - x = 0.05$, masing-masing. Pengukuran kerentanan magnet AC sebagai fungsi suhu dan amplitud medan AC telah dijalankan bagi sampel-sampel yang mengandungi nanozarah Gd_2O_3 pada frekuensi malar f = 333.3 Hz. Dapat diperhatikan bahawa dengan peningkatan kandungan bahan penambah dari x = 0.00 – x = 0.05, suhu permulaan diamagnet berkurangan dari 107 K bagi sampel tulen kepada 97 K bagi kandungan Gd_2O_3 yang akhir. Analisis bagi perbandingan adalah berdasarkan kepada terdapatnya peratus fasa T_C-tinggi (2223) yang lebih tinggi di dalam sampel. Ketumpatan arus genting yang bergantung pada suhu telah diambil daripada data kerentanan AC bagi beberapa sampel terpilih; pengurangan darjah kelakuan diamagnet terhadap medan AC; laju atau perlahannya anjakan puncak kepada suhu lebih rendah dalam $\chi''_{(T)}$ dengan peningkatan amplitud medan dan ketajaman $\chi'_{(T)}$ bagi komponen antara butiran bagi amplitud medan yang sama.

ACKNOWLEDGMENT

In the name of Allah , the most Merciful and the most Gracious. Thanks of Allah, for giving me the strength and will to write and at last complete this thesis.

I am externally grateful to my supervisor, Professor Dr. Abdul Halim Shaari for, most all, believing in me. For all the patience, guidance, advice, ideas, encouragement and continuous discussion, my deepest gratitude goes to you. I also express my regards to my co-supervisor, Dr. Lim Kean Pah and Dr. Chen Soo Kien for their comment, suggestions and guidance throughout the research work.

My special thanks go to Dr. Walter Charles for his helping me on my project, I am grateful to Mr. Rafi for his favors in SEM examination. And my most gratitude to Mr. Zain for X-ray Diffraction, and Mr. Hanif for resistance measurement.

To my friends who never fail to encourage me until the end, Zalita, Hussain, Sewi, Kuan, Hojjat , Maryam, Kazem ,Parisa. I am very thankful to En. Razak and other technical staff in the Physics Department for their technical favors.

To my lovely parents, for their love , support and understanding to keep me going and my brother, Mohammad for his love. And last but not least, to my cousin Bahar and my dear Negar.

I certify that an Examination Committee has met on May 29th, 2009 to conduct the final examination of Saeedeh Sadat Hosseini Ravandi on her Master of Science thesis entitled "Effect of nanoparticulates (Gd_2O_3, Eu_2O_3, Ce_2O_3) addition on properties of $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10}$ ceramics superconductor" in accordance with Universiti Pertanian Malaysia(Higher Degree)Regulation 1981. The Committee recommends that the student be awarded the (Name of relevant degree)

Members of the Examination Committee were as follows:

ELIAS SAION, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

JUMIAH HASSAN, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

HALIMAH MOHAMED KAMARI, PhD
Lecture
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

ROSlAN ABD SHUKOR, PhD
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
Malaysia
(External Examiner)

BUJANG KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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

ABDUL HALIM SHAARI, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

LIM KEAN PAH, PhD
Lecture
Faculty of Science
Universiti Putra Malaysia
(Member)

CHEN SOO KIEN, PhD
Lecture
Faculty of Science
Universiti Putra Malaysia
(Member)

____
HASANAH MOHD GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

DECLARATION

I declare that the thesis is my original work except for quotations and citation 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.

SAEEDEH SADAT HOSSEINI RAVANDI

Date:

TABLE OF CONTENTS

Page

LIST OF TABLES

Tables **Pages**

LIST OF FIGURES

Figures **Pages**

LIST OF PLATES

LIST OF SYMBOLS

T	Temperature
T_C	Critical temperature
$T_{C(on)}$	Onset critical temperature
$T_{C(R=0)}$	Zero resistance temperature
HTS	High T_C superconductor
BCS theory	Bardeen, Cooper and Schrieffer theory
BSCCO	Bi-Sr-Ca-Cu-O superconducting system
Bi(2212)	Family member in $Bi_2Sr_2Ca_nCu_{n+1}O_{6-2n}$, n=1
Bi(2223)	Family member in $Bi_2Sr_2Ca_nCu_{n+1}O_{6-2n}$, n=2
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
H	Applied magnetic field
H_e	External magnetic field
M	Magnetization
a, b, c	Lattice parameters
χ	Susceptibility
χ'	Real part of susceptibility
χ''	Imaginary part of susceptibility
AC	Alternating Current
V	Sample volume
$\mathbf{d}_{hkl}$	Reciprocal *d* vector
hkl	Miller indices

CHAPTER 1

INTRODUCTION

1.1 What is Superconductivity?

Superconductors are materials that have no resistance to the flow of electricity, are one of the last great frontiers of scientific discovery. Not only have the limits of superconductivity has not yet been reached, but the theories that explain superconductivity behavior seem to be constantly under review. In 1911 superconductivity was first observed in mercury (Hg) by Dutch physicist Heike Kamerlingh Onnes. When he cooled it to the temperature of liquid helium, 4 K (-452 F, -269 C), its resistance suddenly disappeared. The Kelvin scale represents an "absolute" scale of temperature. Therefore, it was necessary for Onnes to come within four degrees of the coldest temperature that is theoretically attainable to witness the phenomenon of superconductivity. Later, in 1913, he won a Nobel Prize in physics for his research in this area [Kristiana F, et al ; 2004].

In 1913, the element lead (Pb) was discovered to be superconducting at 7.2 K, this record was broken after 17 years with the element niobium (Nb) with T_C of 9.2 K. later the compounding Nb-Ti alloy was discovered to be superconducting. Among the compounds Nb with other elements, Nb_3Ge had the highest T_C of 22.3 K. The discovery of metals and alloys with zero resistance at low temperatures is an interesting phenomena and has wide applications for the future.

The first widely-accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer. Their theories of Superconductivity, know as the BCS theory, derived from the first letter of each man's last name - and won them a Nobel prize in 1972. The mathematically-complex BCS theory explained superconductivity at temperatures close to absolute zero for elements and simple alloys. The BCS theory describes superconductivity in low temperature metals such as mercury, based on an attractive interaction between electrons due to their coupling with phonon. However, at higher temperatures and with different superconductor systems, the BCS theory has subsequently become inadequate to fully explain how superconductivity is occurring. [Tinkham, et al; 1996]

Then in 1986, a truly breakthrough discovery was made in the field of superconductivity. Alex Müller and Georg Bednorz, researchers at the IBM Research Laboratory in Rüschlikon, Switzerland, created a brittle ceramic compound that superconductor at the highest temperature then known: 30 K. What made this discovery so remarkable was that ceramics are normally insulators. They don't conduct electricity well at all. So, researchers had not considered them as possible high-temperature superconductor candidates. The Lanthanum, Barium, Copper and Oxygen compound that Müller and Bednorz synthesized, behaved in a not-as-yet-understood way. It was later found that tiny amounts of this material were actually superconducting at 58 K, due to a small amount of lead having been added as a calibration standard - making the discovery even more noteworthy.