SYNTHESIS AND CHARACTERIZATIONS OF YBa$_2$Cu$_3$O$_{7-\delta}$ SUPERCONDUCTOR WITH ADDED Al$_2$O$_3$ NANOPARTICLES VIA CITRATE-NITRATE AUTO-COMBUSTION REACTION

MOHD SHAHADAN BIN MOHD SUAN

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2015
UNIVERSITI OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: Mohd Shahadan Bin Mohd Suan (IC No.: 850918-06-5483)
Registration/ Matrix No.: KHA 100026
Name of Degree: The Degree of Doctor of Philosophy
Field of Study: Superconductor Material

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 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 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:

Designation
ABSTRACT

Superconductor materials are renowned to conduct electricity at zero resistance and capable to expel magnetic flux. It can be used in developing efficient wire cables, magnetic energy storage and levitation technologies. Thus, the high temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ with added Al$_2$O$_3$ nanoparticles was synthesized via citrate-nitrate auto-combustion reaction process. The novelty of this research work is the citrate-nitrate auto-combustion reaction method consumed less energy and time compared with other conventional synthesis methods for processing of composite superconductor oxides and produced well distribution of Al$_2$O$_3$ nanoparticles in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor. The auto-combustion reaction transformed the formulated precursor citrate-nitrate gel into very fine ashes. It yielded Al$_2$O$_3$ and YBa$_2$Cu$_3$O$_{7-\delta}$ phases after calcination process which was further heat treated to achieve superconductivity. The reactions during synthesis processes were investigated through the thermal evaluations. The effects of different concentration of Al$_2$O$_3$ nanoparticles on the structure, superconducting, magnetic and mechanical properties of YBa$_2$Cu$_3$O$_{7-\delta}$ were investigated and appraised. The sustained orthorhombic structure in each sample contributed to consistency in superconducting transition temperature while the flux pinning forces provided by the non-superconducting nanoparticles improved the critical current density. Furthermore, the mechanical hardness of the samples was also influenced by the addition of nanoparticles. This work shows that the citrate-nitrate auto-combustion reaction is an effective method to introduce Al$_2$O$_3$ as nanoparticles homogeneously distributed in the YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor.
SINTESIS DAN PENCIRIAN SUPERKONDUKTOR YBa₂Cu₃O₇₋δ DITAMBAH ZARAH NANO Al₂O₃ MELALUI TINDAK BALAS PEMBAKARAN - AUTOMATIK SITRAT-NITRAT.

ABSTRAK

Bahan-bahan superkonduktor telah diketahui dapat mengalirkan arus elektrik pada rintangan sifar dan menyingkir fluks magnet. Ia boleh digunakan dalam membangunkan teknologi wayar kabel efisien, penyimpanan tenaga dan pengapungan magnet. Oleh itu, superkonduktor suhu tinggi YBa₂Cu₃O₇₋δ terkandung zarah nano Al₂O₃ telah disintesis melalui tindak balas pembakaran-automatik sitrat-nitrat. Keaslian kerja penyelidikan ini ialah kaedah sintesis ini lebih menjimatkan tenaga dan masa berbanding kaedah lama dalam penghasilan komposit superkonduktor oksida dan dapat menghasilkan serakan seragam zarah nano Al₂O₃ dalam superkonduktor YBa₂Cu₃O₇₋δ. Pembakaran-automatik telah menukarkan gel sitrat-nitrat yang telah diformulasi kepada abu-abu yang sangat halus. Ianya menjadi fasa-fasa Al₂O₃ dan YBa₂Cu₃O₇₋δ setelah dikalsin sebelum dirawathaba bagi mencapai kesuperkonduksian. Setiap tindak balas yang berlaku semasa proses sintesis ini diperincikan melalui kaedah penilaian terma. Segala kesan akibat penggunaan kepekatan berbeza zarah nano Al₂O₃ terhadap struktur, sifat kesuperkonduksian, kemagnetan dan sifat mekanikal YBa₂Cu₃O₇₋δ dikaji dan ditaksirkkan. Struktur ortorombik setiap sampel menyumbang kepada suhu peralihan kesuperkonduksian yang konsisten manakala daya pengepin yang diperolehi daripada zarah nano bukan superkonduktor telah menambahbaik ketumpatan arus genting. Selain itu, kekerasan mekanikal sampel-sampel juga telah terpengaruh dengan penambahan zarah nano ini. Kajian ini menunjukkan bahawa kaedah pembakaran-automatik sitrat-nitrat merupakan kaedah berkesan untuk menghasilkan Al₂O₃ sebagai bahan zarah nano tertabur secara seragam dalam superkonduktor YBa₂Cu₃O₇₋δ.
ACKNOWLEDGMENT

Foremost I wish to express my sincere appreciation to my supervisor, Dr. Mohd Rafie Johan for his consistent guidance, teaching and supervision during the process of working this research. His advice and comments have helped me significantly in moving forward and completing this thesis report on time. I could not have imagined having better supervisor and mentor during my PhD study.

I would also thank Dr. Yoichi Kamihara from Keio University, Japan for offering me an internship opportunity to work in his research group in Hiyoshi, Japan. This internship program has enlighten me and allowed me to work on diverse exciting project. To my friends in Keio University, you have made my stay in Japan a memorable one.

Besides, I would like to thank my friends in Nanomaterials Group of Advanced Materials lab, Mechanical Engineering of University of Malaya. I thank them for their continuous support and assistance provided whenever I needed a helping hand. A special thanks to Mr. Nazarul Zaman, Mr. Said Sakat and Mrs. Norzirah, a big contribution and assistances from them are very great indeed.

Last but not least, my deepest gratitude goes to my beloved parents, Mohd Suan Tulis and Shariah Dahol and all my siblings, for their endless love and encouragement. I will not be who I am today without their encouragement. Not to forget endless support and understanding from my wife, Vizy Nazira Riazuddin and my little prince, Muhammad Eusoff Muzaffar. To those who indirectly contributed in this research, your kindesses are highly appreciated. Thank you very much.
TABLE OF CONTENTS

ORIGINAL LITERARY WORK DECLARATION ii
ABSTRACT iii
ABSTRAK iv
ACKNOWLEDGEMENTS v
TABLE OF CONTENTS vi
LIST OF FIGURES xi
LIST OF TABLES xvii
LIST OF SYMBOLS AND ABBREVIATIONS xviii

CHAPTER 1: INTRODUCTION 1
1.1 Research background 1
1.2 Problems statement 2
1.3 Research objectives 5
1.4 Scope of the works 6
1.5 Significant of research 7

CHAPTER 2: LITERATURE REVIEW 8
2.0 Superconductivity 8
2.1 Zero resistivity of superconductor 9
2.2 Perfect diamagnetism 11
2.3 Phenomenal theory 13

© Universiti Teknikal Malaysia Melaka
2.3.1 London penetration depth 13
2.3.2 Pippard’s non-local theory 17
2.3.3 Ginzburg-Landau theory 18

2.4 Type II superconductor 21
  2.4.1 Critical current density 21
  2.4.2 Flux pinning 22
  2.4.3 Bean model 24
  2.4.4 Extended Bean model 27

2.5 YBa$_2$Cu$_3$O$_{7-δ}$ superconductor 29
  2.5.1 Addition of nanoparticles in bulk YBa$_2$Cu$_3$O$_{7-δ}$ 32
  2.5.2 Addition of Al$_2$O$_3$ nanoparticles into YBa$_2$Cu$_3$O$_{7-δ}$ 34

2.6 Synthesis of YBa$_2$Cu$_3$O$_{7-δ}$ powder 37

2.7 Synthesis of Al$_2$O$_3$ nanoparticles 38

2.8 Combustion synthesis 39
  2.8.1 Citrate-nitrate auto-combustion reaction 44

CHAPTER 3: METHODOLOGY 49

3.1 Materials 49

3.2 Sample preparation 50
  3.2.1 Citrate to nitrate ratio dependence mixture solution 50
  3.2.2 Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-δ}$ mixture solution 51
  3.2.3 Auto-combustion reaction of the gel 52
  3.2.4 Calcination and sintering process 53

3.3 Characterization technique 55
3.3.1 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) 55
3.2.2 X-ray diffraction (XRD) 55
3.2.3 Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) 57
3.2.4 Resistivity measurement 58
3.2.5 Defining critical temperature ($T_C$) 60
3.2.6 Magnetisation measurement 61
3.2.7 Magnetic critical current density ($J_C$) 62
3.2.8 Hardness test 63
3.2.9 Summary 63

CHAPTER 4: EFFECTS OF CITRATE NITRATE RATIO 65
4.1 Decomposition characteristics 65
4.2 YBa$_2$Cu$_3$O$_{7-\delta}$ structural properties 72
4.3 Microstructure and EDX of YBa$_2$Cu$_3$O$_{7-\delta}$ samples 80
4.4 Critical temperature ($T_C$) analysis 85
4.5 Discussions 87

CHAPTER 5: EFFECTS OF THE ADDITION OF Al$_2$O$_3$ NANOPARTICLES 89
5.1 Decomposition characteristics 89
5.2 Structural properties of Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ 97
5.3 Microstructure and EDX of Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ 108
5.4 Microhardness of Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ 118

5.5 Electrical resistivity and critical temperature ($T_C$) analysis 120

5.6 Magnetic hysteresis and critical current density ($J_C$) analysis 123

5.7 Discussions 130

CHAPTER 6: CONCLUSIONS 132

6.1 Effects of citrate-nitrate ratio 132

6.2 Effects of the addition Al$_2$O$_3$ nanoparticles 132

6.3 Future works 133

REFERENCES 135

LIST OF PUBLICATIONS AND PRESENTED PAPERS 145

Academic Journals 145

Conference Proceedings 146

Conference Presentations 146

APPENDIX A1 147

Refined XRD pattern ($x_{mol} = 0.00$ and $0.02$)

APPENDIX A2 148

Refined XRD patterns ($x_{mol} = 0.04$ and $0.06$)
APPENDIX A3

Refined XRD patterns ($x_{mol} = 0.08$ and $0.10$)
| Figure 2.1 | Progress of $T_C$ according to year discovered (Roslan, 2004). | 9 |
| Figure 2.2 | Temperature dependence $B_C$ relation depicts boundary that separate between superconducting and normal state. | 11 |
| Figure 2.3 | Temperature dependence $B_{C1}$ and $B_{C2}$ of type II superconductor. | 12 |
| Figure 2.4 | Penetration of magnetic field into superconductor, $B(x)$ as determined from equation (2.16). The $B(0)$ is the field on the surface of superconductor. After the $\lambda_L$ of superconductor, $B$ no longer exists. | 17 |
| Figure 2.5 | Internal profiles for the slab superconductor magnetized in a parallel field to its surface of thickness $D$; (a) local fields and (b) current distribution for fields $0$, $H^*/2$, $H^*$ and $2H^*$ (Bean, 1964). | 24 |
| Figure 2.6 | Internal profiles of the slab superconductor after the magnetic field ($H_0$) is removed; (a) local fields, and (b) current distribution (Bean, 1964). | 25 |
| Figure 2.7 | Magnetic hysteresis loop for type II superconductor. $\Delta M$ is the magnetization gap at increased and decreased of magnetic field. | 26 |
| Figure 2.8 | Anisotropic $J_C$ at the magnetic field of $H$ applied perpendicular to surface having of dimensions $l \times t$ (Gyorgy et al., 1989). | 27 |
| Figure 2.9 | Crystal structure of YBa$_2$Cu$_3$O$_{7-\delta}$. | 29 |
Figure 2.10  Lattice parameters for YBa$_2$Cu$_3$O$_{7-\delta}$ with different $\delta$ (Cava et al., 1990).

Figure 2.11  Oxygen deficiencies, $\delta$ dependence $T_C$ for various YBa$_2$Cu$_3$O$_{7-\delta}$ samples.

Figure 2.12  Enthalpy-temperature plot for reactants and products in combustion reaction system (Moore and Feng, 1995).

Figure 3.1  Physical appearance of samples; (a) as-prepared mixture solution, (b) gel, (c) flammable combustion and (d) ashes product.

Figure 3.2  Physical appearances of the resultant powders; (a) before calcination, and (b) after calcination.

Figure 3.3  Pellet sample ready for characterizations after sintering process.

Figure 3.4  Calcination profiles of the ashes product.

Figure 3.5  Sintering profiles of the pellet samples.

Figure 3.6  Rigaku RINT2500Ultra18 XRD machine.

Figure 3.7  Crystal structures are drawn using ‘VESTA 3 program for three-dimensional visualisation of crystal, volumetric and morphology data’ (Momma and Izzumi, 2011).

Figure 3.8  Zeiss Auriga Ultra 40 XB FESEM machine.

Figure 3.9  Sample holder set up for resistivity measurement.

Figure 3.10  Closed cryogen chamber model SRDK-101D.

Figure 3.11  Determination of $T_C$ onset and $T_C$ zero from temperature dependence resistivity curve.

Figure 3.12  Sample holder set up for field dependence magnetization measurement.
Figure 3.13  SQUIDs (Quantum Design Co. LTD; MPMS-XL) for magnetic properties measurement.

Figure 3.14  Flow chart for the preparation and characterization of Al₂O₃ nanoparticles added YBa₂Cu₃O₇ samples.

Figure 4.1  TG/DTA curves of c/n = 0.6 and 0.7 gel samples.

Figure 4.2  TG/DTA curves of c/n = 0.3 and 0.5 gel samples.

Figure 4.3  TG/DTA curves of c/n = 0.9 gel sample.

Figure 4.4  XRD patterns of YBa₂Cu₃O₇₋δ samples after being calcined at 900 °C for 1h.

Figure 4.5  XRD pattern of ashes sample with c/n = 0.6 before calcination.

Figure 4.6  XRD pattern of powder sample with c/n = 0.6 after calcination.

Figure 4.7  Lattice constants of YBa₂Cu₃O₇₋δ samples for different c/n values.

Figure 4.8  Orthorhombicity of YBa₂Cu₃O₇₋δ samples for different c/n values.

Figure 4.9  Crystallite sizes of YBa₂Cu₃O₇₋δ samples for different c/n value.

Figure 4.10  FESEM image of the sample with c/n = 0.3.

Figure 4.11  FESEM images of the sample with c/n = 0.5.

Figure 4.12  FESEM images of the sample with c/n = 0.6.

Figure 4.13  FESEM images of the sample with c/n = 0.7.

Figure 4.14  FESEM images of the sample with c/n = 0.9.

Figure 4.15  EDX spectra of samples for different values of c/n; (a) 0.3, (b) 0.3, (c) 0.6, (d) 0.7 and (e) 0.9.
Figure 4.16: Temperature dependence resistivity of YBa$_2$Cu$_3$O$_{7-\delta}$ samples with different c/n values. 88

Figure 4.17: The $T_C$ onset and $T_C$ zero of the YBa$_2$Cu$_3$O$_{7-\delta}$ samples with different c/n values. 88

Figure 5.1: DTA curves of gel samples having $x_{\text{mol}} = 0.00$ and 0.02. 89

Figure 5.2: TG curves of gel samples having $x_{\text{mol}} = 0.00$ and 0.02. 90

Figure 5.3: DTA curves of Al(NO$_3$)$_3$ added gel samples. 91

Figure 5.4: TG curve of Al(NO$_3$)$_3$ added gel samples. Inset shows TG curves in circle. 94

Figure 5.5: XRD pattern of YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ nanoparticles added YBa$_2$Cu$_3$O$_{7-\delta}$ samples. Black and pink bars at bottom show Bragg diffraction pattern for YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ respectively. 97

Figure 5.6: Refined XRD pattern of sample without Al$_2$O$_3$ nanoparticles ($x_{\text{mol}} = 0.00$). 98

Figure 5.7: Intensity difference patterns for various compositions of Al$_2$O$_3$ nanoparticles added YBa$_2$Cu$_3$O$_{7-\delta}$ samples. 99

Figure 5.8: XRD pattern of Al$_2$O$_3$ ashes. 101

Figure 5.9: XRD pattern of crystalline Al$_2$O$_3$ after calcined at 900 °C for 1h. 101

Figure 5.10: The $a$ and $b$ lattice constants of the samples. Error bars show standard deviation of lattice constant value. 104

Figure 5.11: Orthorhombicity of pure YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$. Error bars show standard deviation of orthorhombicity. 104
Figure 5.12  The $c$ lattice constants of the samples. Error bars show standard deviation of $c$ lattice constant.

Figure 5.13  Crystallite sizes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples.

Figure 5.13  FESEM images of sample with $x_{\text{mol}} = 0.02$.

Figure 5.14  FESEM images of sample with $x_{\text{mol}} = 0.04$.

Figure 5.15  FESEM images of sample with $x_{\text{mol}} = 0.06$.

Figure 5.16  FESEM images of sample with $x_{\text{mol}} = 0.08$.

Figure 5.17  FESEM images of sample with $x_{\text{mol}} = 0.10$.

Figure 5.18  EDX area analysis for $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples;
(a) $x_{\text{mol}} = 0.02$, (b) $x_{\text{mol}} = 0.04$, (c) $x_{\text{mol}} = 0.06$, (d) $x_{\text{mol}} = 0.08$ and (e) $x_{\text{mol}} = 0.10$.

Figure 5.19  EDX spot analysis pointed on nanoparticles; (a) $x_{\text{mol}} = 0.02$, (b) $x_{\text{mol}} = 0.04$, (c) $x_{\text{mol}} = 0.06$, (d) $x_{\text{mol}} = 0.08$ and (e) $x_{\text{mol}} = 0.10$.

Figure 5.20  Microstructure of the intersection of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for sample with $x_{\text{mol}} = 0.06$.

Figure 5.21  Vickers microhardness of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples.

Figure 5.22  Temperature dependence resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples.

Figure 5.23  Critical temperatures of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples.

Figure 5.24  Field dependent magnetization, M-H hysteresis loop of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Al}_2\text{O}_3$ added $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples at 5 K.
Figure 5.25  Field dependent magnetization, M-H hysteresis loop of YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ samples at 77 K.  

Figure 5.26  Magnetic $J_C$ of YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ samples at 5 K.  

Figure 5.27  Magnetic $J_C$ of YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ nanoparticles added YBa$_2$Cu$_3$O$_{7-\delta}$ samples at 77 K.  

Figure 5.28  $J_C$ of YBa$_2$Cu$_3$O$_{7-\delta}$ and Al$_2$O$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ samples at 77K.
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Critical parameters of YBa$_2$Cu$<em>3$O$</em>{7.5}$ superconductor (Roslan, 2004).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.2</td>
<td>$T_C$ and $J_C$ of Al$_2$O$_3$ nanoparticles added YBa$_2$Cu$<em>3$O$</em>{7.5}$ obtained from various studies.</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Comparison of the properties of YBa$_2$Cu$<em>3$O$</em>{7.5}$ produced using various processing techniques (Pathack et al., 2004).</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Raw materials used to prepare stock solutions.</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Citrate-nitrate ratio (c/n) composition.</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Labels of as-prepared solution varied by Al(NO$_3$)$_3$ compositions.</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Temperature dependence decomposition behavior and reaction of the gel samples during auto-combustion reaction.</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Atomic numbers and ratio of the elements obtained from EDX analysis of the YBa$_2$Cu$<em>3$O$</em>{7.5}$ for different c/n values.</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Reaction and weight loss of the Al(NO$_3$)$_3$ added gel samples at varied steps.</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Elemental analysis of YBa$_2$Cu$<em>3$O$</em>{7.5}$ structure and Al$_2$O$_3$ nanoparticles in each Al$_2$O$_3$ added YBa$_2$Cu$<em>3$O$</em>{7.5}$ samples.</td>
</tr>
</tbody>
</table>
## LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>lattice constant at $x$ direction</td>
</tr>
<tr>
<td>$A$</td>
<td>cross section of the sample</td>
</tr>
<tr>
<td>$b$</td>
<td>lattice constant at $y$ direction</td>
</tr>
<tr>
<td>$B_a$</td>
<td>applied magnetic field</td>
</tr>
<tr>
<td>$B_C$</td>
<td>critical magnetic field</td>
</tr>
<tr>
<td>$B_i$</td>
<td>interior magnetic field</td>
</tr>
<tr>
<td>$B_r$</td>
<td>remnant flux density</td>
</tr>
<tr>
<td>$c$</td>
<td>lattice constant at $z$ direction</td>
</tr>
<tr>
<td>$c/n$</td>
<td>citrate to nitrate ratio</td>
</tr>
<tr>
<td>SSP</td>
<td>solid-state processing</td>
</tr>
<tr>
<td>$C_p$</td>
<td>heat capacity</td>
</tr>
<tr>
<td>CP</td>
<td>co-precipitation</td>
</tr>
<tr>
<td>$d$</td>
<td>grain size</td>
</tr>
<tr>
<td>$D$</td>
<td>thickness of slab</td>
</tr>
<tr>
<td>$\delta$</td>
<td>oxygen deficiency</td>
</tr>
<tr>
<td>DTA</td>
<td>differential thermal analysis</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
</tr>
<tr>
<td>$E_F$</td>
<td>fermi energy</td>
</tr>
<tr>
<td>emf</td>
<td>electromotive force</td>
</tr>
<tr>
<td>FESEM</td>
<td>field emission scanning electron microscope</td>
</tr>
<tr>
<td>$F_L$</td>
<td>Lorentz force</td>
</tr>
</tbody>
</table>
$F_n$  free energy at normal state

$F_p$  pinning force

$f_p$  basic pinning force

$F_s$  free energy at superconducting state

$H(P)$  heat required by products

$H(R)$  heat required by reactants

$B_{C1}, H_C$  critical magnetic field

$B_{C2}, H_{C2}$  upper critical applied magnetic field

$H_V$  Vickers hardness

$J_C$  critical current density

$J_s$  density of superconducting current

$k_B$  Boltzmann’s constant

$l$  length of superconductor slab

$L$  Phase transformation enthalpy

$m$  mass of electron

$MO$  metal oxide

$MOH$  metal hydroxide

$MPMS$  magnetic properties measurement system

$n_i$  stoichiometry ratio of reactants coefficient

$n_j$  stoichiometry ratio of products coefficient

$n_n$  number of normal electron

$n_o$  average number of electrons

$N_p$  pinning center density

$n_s$  number of superconducting electron

$P_j$  products

$\Phi_o$  flux quantum
R

\text{resistance}

R_i

\text{reactants}

RT

\text{room temperature}

\text{SQUIDs}

\text{superconducting Quantum Interference Devices}

t

\text{width of superconductor slab}

T_0

\text{initial temperature}

T_{ad}

\text{adiabatic temperature}

T_C

\text{superconductor critical temperature}

T_{com}

\text{combustion temperature}

\text{TGA}

\text{thermogravimetric Analysis}

T_{ig}

\text{ignition temperature}

U_o

\text{flux creep potential}

U_p

\text{flux pinning potential}

V_i

\text{volume fraction of pinning center}

v_s

\text{velocity of superconducting electron}

x_{mol}

\text{concentration of Al}_2\text{O}_3\ \text{nanoparticles in the sample}

\text{XRD}

\text{X-ray diffraction}

\text{YSZ}

\text{yttrium stabilized zirconia}

\Delta E

\text{energy gap of Cooper pair fluid}

\Delta H

\text{heat needed for ignition}

\Delta M

\text{magnetization gap}

\Delta Q

\text{heat loss}

\lambda

\text{penetration depth}

\mu_r

\text{relative permeability}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi$</td>
<td>superconductors coherence length</td>
</tr>
<tr>
<td>$\xi_{ab}$</td>
<td>coherence length parallel to $a$-$b$ plane</td>
</tr>
<tr>
<td>$\xi_c$</td>
<td>coherence length parallel to $c$ plane</td>
</tr>
<tr>
<td>$\xi_0$</td>
<td>intrinsic coherence length</td>
</tr>
<tr>
<td>$\rho$</td>
<td>resistivity</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity</td>
</tr>
<tr>
<td>$\tau$</td>
<td>crystallite size</td>
</tr>
<tr>
<td>$\psi$</td>
<td>superconducting order parameter</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Ginzburg-Landau parameter</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Research background

Superconductivity is a promising technology to prevent energy losses attributed from electrical resistivity. This technology attracts much attention to the researches due to two main reasons: the electricity can be conducted at zero resistivity and the magnetic flux can be totally repelled out from the body of superconducting material. Since discovered in 1911, superconductivity was only been found in elements and alloys where the critical temperature \( T_C \) of these materials are very low (Onnes, 1991). In 1986, the lanthanum cuprate was found to be the first compound material to exhibit superconductivity (Muller and Bednorz, 1986). This breakthrough was followed by discovery of yttrium barium copper oxide \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) superconducting compound in 1987 which brought a great excitement within the scientific community because this material can conduct electricity without having resistivity at temperatures above 77 K. This is the temperature at which nitrogen liquefies, thus \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) changed the perspective of the applications of superconductivity and opened up the possibility for numerous advancements of technologies (Wu et al., 1987).

Categorized as type II superconductor, \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) shows perfect diamagnetism at below lower critical fields \( H_{C1} \), allows penetration of quantized magnetic flux (vortex) at higher fields, and loss superconductivity at above higher critical fields \( H_{C2} \). It means that the coherence of superconducting state is preserved even in the presence of weak currents and magnetic fields below \( H_{C2} \), and makes it
practical to be used in stronger magnetic fields compared with conventional superconductors.

1.2 Problems statement

Theoretically, YBa$_2$Cu$_3$O$_{7-\delta}$ has excellent ability to carry higher critical current density ($J_C$) due to having very high $H_{C2}$ compared with $H_{C1}$. However, when electrical current is flowed in applied magnetic field of $H_{C1} < H < H_{C2}$, the interaction between vortex and current flow results in the motion of vortex due to Lorentz force which can cause energy loss. At this point, only a small density of current limits by $J_C$ is permitted to flow through this superconductor before losing energy. Generally the $J_C$ can be increased if the vortex is prevented from moving. This can be achieved by pinning them with suitable non-superconducting point as known as pinning centre materials. Pinning centre materials in YBa$_2$Cu$_3$O$_{7-\delta}$ can be created either by inducing defects through irradiation techniques and chemical doping or by introducing second phase particles having nanometer size. In chemical doping, elements such as calcium (Ca), potassium (K), silver (Ag) and aluminium (Al) are diffused into YBa$_2$Cu$_3$O$_{7-\delta}$ structure (Giri et al., 2005, Celebi et al., 2000, Sen et al., 1990 and Zhang et al., 1995). These elements locally modify the crystallinity of the structure and generate defects such as twins, tweed, and inhomogeneous micro-defects to pin the vortices. The $J_C$ can be improved by chemical doping but in return this method may reduce the $T_C$, since the orthorhombicity of YBa$_2$Cu$_3$O$_{7-\delta}$ is being altered; hence, decreased.

Thus for some reasons, introduction of nanoparticles in YBa$_2$Cu$_3$O$_{7-\delta}$ has generated a great interest among researchers. This method represents an easy controlled, non-destructive and efficient tool for improving the mechanical, structural and
superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds. Various nanometer particles; such as, silicon carbide (SiC), zirconia ($\text{ZrO}_2$), yttrium oxide ($\text{Y}_2\text{O}_3$), cerium dioxide ($\text{CeO}_2$), tin oxide ($\text{SnO}_2$) and aluminum oxide or Alumina ($\text{Al}_2\text{O}_3$) has been reported to add into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. All of these nanoparticles were acted as additional pinning centre and resulted in an increase of the $J_C$ in higher magnetic fields (Guo et al., 1999, Zhang and Evetts, 1993, Goswami et al., 2007, Lee et al., 2001, He et al., 2001 and Mellekh et al., 2006). In order to effectively pin the vortices, nanoparticles should possess features including high density or uniform distribution. Nanoparticles having size of 3-10 nm is equal to the coherence length ($\xi$) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and able to be located at CuO$_2$ planes (Moutalibi and M’chirgui, 2007).

Among the added nanoparticles, $\text{Al}_2\text{O}_3$ is more attractive to be selected as the pinning centre material in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Beside the capability to pin the vortex motions, $\text{Al}_2\text{O}_3$ nanoparticles are also selected due to its availability in nanometer size, easy fabrication route, higher thermal stability, higher density, better hardness and lower cost. In 1987, the effects of Al substitution for yttrium (Y) or copper (Cu) sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were accidently found. For long period of high temperature calcination process, the use of alumina crucibles results in the incorporation of Al in crystals having composition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{Al}_x\text{O}_y$. X-ray diffraction (XRD) analysis reveals that such substitution does not lead to changes in the structural symmetry of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ but the orthorhombicity of the system is decreased with increasing Al content (Zhang et al., 2005). The value of $T_C$ decreases with increasing Al. This finding was confirmed by Zhang and his colleagues as they purposely added $\text{Al}_2\text{O}_3$ powder into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ but yet no reports have published regarding the ability of $\text{Al}_2\text{O}_3$ particles as pinning centre material. Until Mellekh et al. (2006) revealed that by using the $\text{Al}_2\text{O}_3$ nanoparticles with size about 50 nm, the $J_C$ of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was significantly improved. The improvement