UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF YBa_2Cu_4O8 SUPERCONDUCTOR AND ANALYSIS OF ELECTRONIC PROPERTIES IN COMPARISON TO OTHER YBCO FAMILY COMPOUNDS

CHEONG CHOON MIN

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By

CHEONG CHOON MIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS OF $YBa_2Cu_4O_8$ SUPERCONDUCTOR AND ANALYSIS OF ELECTRONIC PROPERTIES IN COMPARISON TO OTHER YBCO FAMILY COMPOUNDS

By

CHEONG CHOON MIN

September 2020

Chairman: **Chen Soo Kien, PhD**
Faculty : **Science**

In recent years, high-temperature superconductor YBCO has been recognized for developing secondary generation of coated superconductor for various technological applications due to its high transition temperature, T_c. $YBa_2Cu_4O_8$ (Y124) with stoichiometric oxygen content is able to maintain Y124 phase before decomposing to $YBa_2Cu_3O_{7-x}$ (Y123) and CuO phases at temperature above 850 ^oC. This ascendancy of thermal stability overtook Y123 in practical applications. To date, a relatively pure $YBa_2Cu_4O_8$ sample had been successfully prepared by heat treatment in high-oxygen-pressure [1-4] or using wet methods [5-9] with heat treatment at ambient pressure. For $YBa_2Cu_4O_8$ samples prepared by solid state reaction method at ambient pressure, either multiple grindings with repeated heat treatment [10] or usage of additional technique is required to improve the synthesis condition [11-18]. It was reported that $YBa_2Cu_4O_8$ could be synthesized within hours at temperature around 1000 ^oC and pressure above 50 bar [1-4]. The equipment for high pressure technique is expensive and could bring about safety issues. Although the wet methods do not rely on high pressure, several processes before heat treatments is required and the sintering time is about 3-5 days with few intermittent grinding [5-9]. Solid state reaction methods offer relatively lower cost and simpler procedure as compared with the high pressure techniques and the wet methods. However, synthesis of $YBa_2Cu_4O_8$ without using special treatment requires very long sintering time [10]. With the help of alkali enhancer, the sintering time of solid state reaction method is reduced to almost that of the wet methods [11,16]. Nonetheless, the sintering time and the fraction of $YBa_2Cu_4O_8$ phase and impurities within the samples obtained for those solid state reaction methods are still ambiguous. Moreover, limited studies have been conducted to synthesize $YBa_2Cu_4O_8$ by starting materials of $YBa_2Cu_3O_{7-x}$ and CuO [14]. On the other hand, the electronic properties of the two similar structures of Y123 and Y124 are diverse in certain situation. For example, their superconducting properties are diverse when they are doped with calcium. With calcium substitution, the $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ improved the superconducting current density limit

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but suppressed the superconducting transition temperature [19-21]. On the contrary, the T_c of $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ was improved to 90 K by 10.0% of calcium doped on the yttrium site [22-28]. The dependency of T_c on hole densities was observed in cuprate superconductor [29-32]. However, to determine hole densities of YBCO is non-trivial. Tallon et al. [32] used rather complicated bond-valence-sum (BVS) method to calculate the hole densities for Y123. Hence, it is urged to calculate the hole densities based on density functional theory and investigate the electronic band structure of YBCO family compound and obtain its relation to the superconducting transition temperature. This thesis was focused on the synthesis and electronic properties of Y124 phase with comparison to other YBCO family compounds. This thesis began with the study of preparation of Y124 phase by solid state reaction method with heat treatment at 1 atm oxygen pressure. X-ray diffraction technique was used to identify the phases formed and the crystal structure of Y124. Scanning electron microscope was used in order to investigate grain morphology of the samples. Thermogravimetric analysis was performed to study the thermal stability of the sample. Electrical properties of the samples were measured using the four-point probe technique.

Six samples were prepared using nitrate precursors and one sample was prepared by carbonate precursor. This study was to understand the Y124 phase formation and its formation rate. From the study, it could be summarized that; Y124 phase could form if the oxide precursors underwent the heat treatment environment in favour of Y124 and the secondary oxides would persist in sample, hence clean single phase Y124 was difficult to produce. Next, starting powders tetragonal-Y123 and CuO were used to prepare Y124. Tetragonal-Y123 is obtained by heat treatment on Y123 power at 850 ^oC in argon gas flow for 12 hours. However, the results indicate that getting tetragonal-Y123 first is an unnecessary step. Following, Y124 was prepared directly from starting powders Y123 and CuO. By this way, significant Y124 phase was obtained after 2nd heat treatment. The lattice parameters of the synthesized Y124 were then adopted in the simulation study to analyse the electronic band structure of Y124 using density functional theory. The simulation works employed the Quantum Espresso computation package. The Y124 together with YBCO family compounds Y1236 ($YBa_2Cu_3O_6$), Y12365 ($YBa_2Cu_3O_{6.5}$), Y1237 ($YBa_2Cu_3O_7$) and Ca-doped YBCO compounds YCa123 ($Y_{0.875}Ca_{0.125}Ba_2Cu_3O_7$), YCa124 ($Y_{0.875}Ca_{0.125}Ba_2Cu_4O_8$) were investigated. Structural optimization was obtained for all compounds using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The orthorhombicity of Y124 and Y123 compounds (Y1236, Y12365, and Y1237) agreed with the trend of T_c, where compounds with higher T_c in practice have higher orthorhombicity, however, this is not so for Ca-doped compounds. By analysing the atoms in Cu-O_2 plane, Cu(2) and O(3) are moved further away from the yttrium (Y) atom for compounds with higher T_c. For Y12365 and Y1237, O(2) remained on the same level. Ca with about the same atomic radius as Y did not affect much the lattice constant and volume of the compounds. However, Ca^{2+} with less electronegative as compared with Y^{3+} modified the electronic properties of the region within the bilayers Cu-O_2 plane. The calculations including band structure, density of state and charge density of the Y124 and other YBCO family compounds were then performed accordingly. The density of state at Fermi level, $N(E_F)$ and number of holes of Cu(2) and Cu-O_2 showed tendency of increment consistent with the T_c of the compounds except for YCa123. Y124 with double Cu-O chains has 4.80 holes per unit cell that is higher than the Y1237 which has 3.52 holes per unit cell, but the number of holes at its Cu(2) and

Cu-O_2 plane are lower than the Y1237. For example, the number of holes at Cu(2) and Cu-O_2 plane of Y124 are 0.60 and 1.07 respectively that is lower than Y1237 that have 0.66 holes per Cu(2) and 1.19 holes per Cu-O_2 plane. Y1237 and YCa124 with T_c of around 90 K have the same number of holes in Cu(2) and Cu-O_2 which are 0.66 and 1.19 respectively. The hole densities in Cu-O_2 plane showed good agreement with the results of the $N(E_F)$, number of holes per Cu(2) and number of holes per Cu-O_2, except for YCa124 and Y1237. Y124 and YCa124 have highest hole densities in the unit cell which are 2.33 and 2.37 respectively. However, the hole densities in Cu-O_2 plane of Y124 is less than that of Y1237 which are 4.07 and 4.50 respectively. For YCa124 that has about the same T_c with Y1237, their hole densities in Cu-O_2 plane is very close which are 4.56 and 4.50 respectively. In summary, the simulation studies showed that the coordinates of atoms at Cu-O_2 plane and orthorhombicity could not be really related to the superconducting transition temperature of the compounds. However, the hole values on the Cu(2) atom and Cu-O_2 plane did show a satisfactory relationship with the superconducting transition temperature.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS $YBa_2Cu_4O_8$ SUPERKONDUKTOR DAN ANALISIS SIFAT ELEKTRONIK DENGAN PERBANDINGAN DENGAN SEBATIAN KELUARGA YBCO

Oleh

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Dalam tahun-tahun kebelakangan ini, superkonduktor suhu tinggi YBCO telah diakui untuk mengembangkan generasi kedua superkonduktor bersalut untuk pelbagai aplikasi teknologi kerana suhu peralihannya, T_c yang tinggi. $YBa_2Cu_4O_8$ (Y124) dengan kandungan oksigen stoikoimetrik mampu mengekalkan fasa Y124 sebelum terurai kepada fasa $YBa_2Cu_3O_{7-x}$ (Y123) dan CuO pada suhu melebihi 850 ^oC. Peningkatan kestabilan terma ini mengatasi Y123 dalam aplikasi praktikal. Sehingga kini, sampel $YBa_2Cu_4O_8$ yang agak tulen berjaya disiapkan dengan rawatan haba dalam tekanan oksigen tinggi [1-4] atau menggunakan kaedah basah [5-9] dengan rawatan haba pada tekanan ambien. Untuk sampel $YBa_2Cu_4O_8$ yang disediakan dengan kaedah tindak balas keadaan pepejal pada tekanan ambien, baik beberapa penggilingan dengan rawatan haba berulang [10] atau penggunaan teknik tambahan diperlukan untuk memperbaiki keadaan sintesis [11-18]. Dilaporkan bahawa $YBa_2Cu_4O_8$ dapat disintesis dalam beberapa jam pada suhu sekitar 1000 ^oC dan tekanan di atas 50 bar [1-4]. Peralatan untuk teknik tekanan tinggi itu mahal dan boleh menimbulkan masalah keselamatan. Walaupun kaedah basah tidak bergantung pada tekanan tinggi, beberapa proses sebelum rawatan haba diperlukan dan masa pensinteran adalah sekitar 3-5 hari dengan beberapa penggilingan berselang [5-9]. Kaedah tindak balas keadaan pepejal menawarkan kos yang lebih rendah dan prosedur yang lebih sederhana berbanding dengan teknik tekanan tinggi dan kaedah basah. Walau bagaimanapun, sintesis $YBa_2Cu_4O_8$ tanpa menggunakan rawatan khas memerlukan masa pensinteran yang sangat lama [10]. Dengan bantuan penambah alkali, masa tindak balas kaedah tindak balas keadaan pepejal dikurangkan menjadi hampir sama dengan kaedah basah [11,16]. Walaupun begitu, masa pensinteran dan pecahan fasa $YBa_2Cu_4O_8$ dan kekotoran dalam sampel yang diperoleh untuk kaedah tindak balas keadaan pepejal itu masih tidak jelas. Lebih-lebih lagi, kajian terhad telah dilakukan untuk mensintesis $YBa_2Cu_4O_8$ dengan memulakan bahan $YBa_2Cu_3O_{7-x}$ dan CuO [14]. Selain itu, sifat elektronik dari dua struktur serupa Y123 dan Y124 berbeza dalam keadaan tertentu. Sebagai contoh, sifat superkonduktornya adalah berbeza apabila

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didoping dengan kalsium. Dengan penggantian kalsium, $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ meningkatkan had ketumpatan arus superkonduktor tetapi menekan suhu peralihan superkonduktor [19-21]. Sebaliknya, T_c $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ ditingkatkan kepada 90 K dengan 10.0% kalsium yang didop pada laman yttrium [22-28]. Ketergantungan T_c pada ketumpatan lubang diperhatikan dalam superkonduktor cuprate [29-32]. Walau bagaimanapun untuk menentukan ketumpatan lubang YBCO tidak sederhana. Tallon et al. [32] menggunakan kaedah bond-valence-sum (BVS) yang agak rumit untuk mengira ketumpatan lubang bagi Y123. Oleh itu, digesa untuk mengira ketumpatan lubang berdasarkan teori fungsian ketumpatan dan untuk menyelidiki struktur jalur elektronik kompaun keluarga YBCO dan mendapatkan kaitannya dengan suhu peralihan superkonduktor. Tesis ini difokuskan pada sintesis dan sifat elektronik fasa Y124 dengan perbandingan dengan sebatian keluarga YBCO yang lain. Tesis ini dimulakan dengan kajian penyediaan fasa Y124 dengan kaedah tindak balas keadaan pepejal dengan rawatan haba pada tekanan oksigen 1 atm. Teknik difraksi sinar-X digunakan untuk mengenal pasti fasa yang terbentuk dan struktur kristal Y124. Mikroskop elektron imbasan digunakan untuk menyiasat morfologi sampel. Analisis termogravimetri dilakukan untuk mengkaji kestabilan terma sampel. Sifat elektrik sampel diukur dengan menggunakan teknik probe empat titik.

Enam sampel disediakan menggunakan prekursor nitrat dan satu sampel disediakan oleh prekursor karbonat. Kajian ini adalah untuk memahami pembentukan fasa Y124 dan kadar pembentukannya. Dari kajian tersebut, kita dapat merumuskan bahawa; Fasa Y124 dapat terbentuk jika prekursor oksida menjalani persekitaran perlakuan panas yang memihak kepada Y124 dan oksida sekunder akan bertahan dalam sampel, oleh itu fasa tunggal bersih Y124 sukar dihasilkan. Seterusnya, serbuk permulaan tetragonal-Y123 dan CuO digunakan untuk menyiapkan Y124. Tetragonal-Y123 diperoleh dengan rawatan haba pada kuasa Y123 pada suhu 850 ^oC dalam aliran gas argon selama 12 jam. Walau bagaimanapun, hasilnya menunjukkan bahawa mendapatkan tetragonal-Y123 terlebih dahulu adalah langkah yang tidak perlu. Berikutan, Y124 disiapkan secara langsung dari serbuk permulaan Y123 dan CuO. Dengan cara ini, fasa Y124 yang signifikan diperolehi selepas rawatan panas ke-2 Parameter kisi dari Y124 yang disintesis kemudian diadopsi dalam kajian simulasi untuk menganalisis struktur jalur elektronik Y124 menggunakan teori fungsian ketumpatan. Kerja-kerja simulasi menggunakan pakej pengiraan Quantum Espresso. Sebatian Y124 bersama keluarga YBCO Y1236 ($YBa_2Cu_3O_6$), Y12365 ($YBa_2Cu_3O_{6.5}$), Y1237 ($YBa_2Cu_3O_7$) dan sebatian YBCO Ca-doped YCa123 ($Y_{0.875}Ca_{0.125}Ba_2Cu_3O_7$), YCa124 ($Y_{0.875}Ca_{0.125}Ba_2Cu_4O_8$) telah disiasat. Pengoptimuman struktur diperoleh untuk semua sebatian menggunakan algoritma Broyden-Fletcher-Goldfarb-Shanno (BFGS). Orthorhombisiti sebatian Y124 dan Y123 (Y1236, Y12365, dan Y1237) bersetuju dengan trend T_c, di mana sebatian dengan T_c yang lebih tinggi dalam praktiknya mempunyai orthorhombisiti yang lebih tinggi, namun, ini tidak berlaku pada sebatian Ca-doped. Dengan menganalisis atom-atom dalam satah Cu-O_2, Cu(2) dan O(3) dipindahkan lebih jauh dari atom yttrium (Y) untuk sebatian dengan T_c yang lebih tinggi. Untuk Y12365 dan Y1237, O(2) kekal pada tahap yang sama. Ca dengan jejari atom yang hampir sama dengan Y tidak banyak mempengaruhi pemalar kisi dan isipadu sebatian. Walau bagaimanapun, Ca^{2+} dengan elektronegatif yang lebih rendah dibandingkan dengan Y^{3+} mengubah sifat elektronik dalam sekeliling dwi-lapisan Cu-O_2. Pengiraan termasuk struktur jalur, ketumpatan keadaan dan ketumpatan cas Y124 dan sebatian keluarga YBCO yang lain kemudian

dilakukan dengan sewajarnya. Ketumpatan keadaan pada tahap Fermi, $N(E_F)$ dan bilangan lohong Cu(2) dan Cu-O_2 menunjukkan kecenderungan kenaikan yang konsisten dengan T_c sebatian kecuali untuk YCa123. Y124 dengan rantai Cu-O berganda mempunyai 4.80 lohong per sel unit iaitu lebih tinggi daripada Y1237 yang mempunyai 3.52 lohong per sel unit, tetapi jumlah lohong pada satah Cu(2) dan Cu-O_2nya lebih rendah daripada Y1237. Contohnya, bilangan lohong pada satah Cu(2) dan Cu-O_2 Y124 adalah 0.60 dan 1.07 masing-masing iaitu lebih rendah daripada Y1237 yang mempunyai 0.66 lohong per Cu(2) dan 1.19 lohong per satah Cu-O_2. Y1237 dan YCa124 dengan T_c sekitar 90 K mempunyai bilangan lohong yang sama di Cu(2) dan Cu-O_2 dengan 0.66 dan 1.19 masing-masing. Ketumpatan lohong di satah Cu-O_2 menunjukkan persetujuan yang baik dengan hasil $N(E_F)$, bilangan lohong per Cu(2) dan jumlah lohong per Cu-O_2, kecuali untuk YCa124 dan Y1237. Y124 dan YCa124 mempunyai ketumpatan lohong tertinggi di sel unit yang masing-masing adalah 2.33 dan 2.37. Walau bagaimanapun, ketumpatan lohong pada satah Cu-O_2 Y124 adalah kurang daripada Y1237 yang masing-masing 4.07 dan 4.50. Untuk YCa124 yang mempunyai T_c yang hampir sama dengan Y1237, ketumpatan lohong mereka di satah Cu-O_2 sangat dekat iaitu masing-masing 4.56 dan 4.50. Ringkasnya, kajian simulasi menunjukkan bahawa koordinat atom pada satah Cu-O_2 dan orthorhombisiti tidak dapat benar-benar berkaitan dengan suhu peralihan superkonduktor sebatian. Walau bagaimanapun, nilai lohong pada atom Cu(2) dan atom Cu-O_2 menunjukkan hubungan yang memuaskan dengan suhu peralihan superkonduktor.

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LIST OF SYMBOLS AND ABBREVIATIONS

HTSC	High temperature superconductor
YBCO	Yttrium barium copper oxide
BLCO	Barium lanthanum copper oxide
BSCCO	Bismuth strontium calcium copper oxide
HBCCO	Mercury barium calcium copper oxide
TBCCO	Thallium barium calcium copper oxide
Y123	$YBa_2Cu_3O_{7-x}$
Y124	$YBa_2Cu_4O_8$
Y247	$Y_2Ba_4Cu_7O_{15}$
Y1236	$YBa_2Cu_3O_6$
Y12365	$YBa_2Cu_3O_{6.5}$
Y1237	$YBa_2Cu_3O_7$
Ca1237	$CaBa_2Cu_3O_7$
Ca124	$CaBa_2Cu_3O_8$
XRD	X-ray diffraction
SEM	scanning electron microscope
FESEM	Field emission scanning electron microscope
TEM	Transmission electron microscopy
VSM	Vibrating sample magnetometer
TGA	Thermogravimetric analysis
SQUID	Superconducting quantum interference device
T_c	Critical transition temperature
$T_{c,max}$	Maximum critical transition temperature
λ_{ep}	Electron-phonon coupling parameter
ω_D	Debye frequency
V_{eff}	Effective potential between electrons
ω	Frequency of mobile electrons
ρ	Resistivity
J_c	Superconducting critical current density
J_{CL}	Depairing critical current
$\boldsymbol{J}$	Current density
$\boldsymbol{J_s}$	Superconducting current density
n_s	Superconducting carrier density
λ	Penetration depth
ξ	Coherent length
κ	Ginzburg-Landau parameter
$\boldsymbol{B}$	Magnetic flux density
$\boldsymbol{H}$	Magnetic field intensity
$\boldsymbol{h}$	Microscopic magnetic field intensity
Δ	Energy gap
B_c	Critical magnetic field
B_{c1}	Lower critical magnetic field of type-II superconductor
B_{c2}	Upper critical magnetic field of type-II superconductor
h	Plank's constant
Φ_o	Flux quantum

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Ry	Rydberg unit of energy
Bohr	Bohr radius
DFT	Density functional theory
$N(E_F)$	Density of state at Fermi energy
P	Hole concentration
r_o	Characteristic length
r_i	Inter-atomic distance
V_{atom}	Oxidation number of an atom

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CHAPTER 1

INTRODUCTION

1.1 Background of superconductor

Superconductivity is a remarkable property of a substance. Superconductor with its immense capabilities would greatly enhance the advancement of science and technology, from consumer level to high-tech industries.

Superconductivity can be used in many aspects. Gupta et al. [33] and Silver et al. [34] comprehensively reviewed the application of superconductor in various fields including in power generator, electronics and communications, digital storage, and medical applications. The most direct sense from superconductor is its DC zero resistivity can be used in the electrical power industries. For example, the "supercable" - a superconducting cable used for conducting electricity. Using the supercable as transmission line in electric power transmission system can reduce power loss and overall cost for the system. At present, AC transmission system operates at high voltage for effectively power transmission, and required a couple of transformers to step down the voltage level before the usage by end user. These transformers are costly in converting hundred-thousands of volts to consumer voltage level. A transmission system based on supercable can operate at relatively lower voltage level, in which DC transmission system could be used instead of AC system. This would greatly reduce the construction and operation cost for the current transmission system. The other potential application of superconductor in power industry is power station. Unlike supercable using its 'perfect conductivity', power station uses large magnetic field generated by superconducting coil. Superconducting wire allows the flow of much higher current than the normal conductor; therefore, high magnetic field intensity can be generated from the superconducting coil. In fact, most of the current applications of superconductor are to generate high magnetic field intensity, for instance, magnetic resonance imaging, nuclear magnetic resonance, and particle accelerator.

Another property of superconductor is Meissner effect. A superconductor in superconducting state exhibits perfect diamagnetism where the interior of the material expulses external magnetic field. This phenomenon is deviated from the classical theory of 'prefect conductor' and is totally unexpected before the discovery of superconductivity. With this Meissner effect, a superconductor can be levitated by magnetic field through flux pinning phenomenon. Therefore, a safe and reliable maglev train can then be designed accordingly.

Superconductor is also a material that manifests quantum mechanical behaviour, in which supercurrent from one superconductor is able to tunnel to another superconductor when they are placed closely but without any electrical contact. This phenomenon is

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called Josephson Effect. Josephson Effect is employed in fast switching electronic systems and high magneto-sensitivity devices like SQUID.

The potentials of superconductor are still yet to be fully materialized. With continued advances in research, superconductivity can lead to a new era of revolution in science and technology.

1.2 Problem statement

Since the discovery of yttrium-barium-copper-oxide superconductor, enormous research has been focused on investigating the compound $YBa_2Cu_3O_{7-\delta}$. It is the material which has been recognized for its ease of sample preparation and with adequate temperature margin over the boiling point of liquid nitrogen. $YBa_2Cu_4O_8$ has higher thermal stability may serve as a better candidate for applications, yet little attention has been paid to this compound. The limitation of $YBa_2Cu_4O_8$ compared with $YBa_2Cu_3O_{7-\delta}$ is clear – the former does not have adequate temperature margin over the boiling point of liquid nitrogen. However, Ca doping has proven to be able to improve the superconducting transition temperature of $YBa_2Cu_4O_8$ to 90 K [22-28].

So far, a relatively pure $YBa_2Cu_4O_8$ sample had been successfully prepared by heat treatment in high-oxygen-pressure [1-4] or using wet methods [5-9] with heat treatment at ambient pressure. For $YBa_2Cu_4O_8$ samples prepared by solid state reaction method at ambient pressure, either multiple grindings with repeated heat treatment [10] or usage of additional technique is required to improve the synthesis condition [11-18]. It was reported that $YBa_2Cu_4O_8$ with an extra Cu-O chain compared with $YBa_2Cu_3O_7$ could be synthesized within hours at temperature around 1000 ^oC and oxygen pressure above 50 bar [1-4]. The equipment for high pressure technique is expensive and could bring about safety issues. Although the wet methods do not rely on high pressure, several processes before heat treatments is required and the sintering time is about 3-5 days with few intermittent grinding [5-9]. Solid state reaction methods offer relatively lower cost and simpler procedure as compared with the high pressure techniques and the wet methods. However, synthesis of $YBa_2Cu_4O_8$ without using special treatment requires very long sintering time [10]. With the help of alkali enhancer, the sintering time of solid state reaction method is reduced to almost that of the wet methods [11,16]. Solid state reaction method is usually performed by mixing the related metal carbonate oxides or metal nitrogen oxides as starting materials [11-13, 16-18]. Moreover, limited study has been conducted to synthesize $YBa_2Cu_4O_8$ by starting materials of $YBa_2Cu_3O_{7-x}$ and $Cu\text{-}O_2$ [14]. The preparation of $YBa_2Cu_4O_8$ by $YBa_2Cu_3O_{7-x}$ and $Cu\text{-}O_2$ as starting materials is relatively simpler and shorter sintering time is required. Nonetheless, the sintering time and the fraction of $YBa_2Cu_4O_8$ phase and impurities within the samples obtained for those solid state reaction methods are still ambiguous.

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$YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$ have a similar lattice structure; hence they have a similar electronic band structure. However, their superconducting properties are diverse when they are doped with calcium. It was reported that the substitution of calcium on yttrium site of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ improved the superconducting current density limit but suppressed the superconducting transition temperature [19-21]. On the contrary, the T_c of $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ was improved to 90 K by 10% of calcium doped on the yttrium site [22-28]. Hence, to understand these contrary behaviour of superconducting, it is interested to investigate the electronic band structure of Ca-doped $YBa_2Cu_3O_{7-\delta}$ and Ca-doped $YBa_2Cu_4O_8$ and to compare with other YBCO members like $YBa_2Cu_4O_8$, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.5}$, and $YBa_2Cu_3O_6$.

1.3 Objectives of the study

The purpose of this research project is (i) to synthesize $YBa_2Cu_4O_8$ with different approach using solid state reaction method and (ii) to undertake simulation study on the electronic band structure of $YBa_2Cu_4O_8$ and other YBCO family members.

Properties of the synthesized samples are studied through characterization using X-ray diffraction, thermogravimetric analyser, scanning electron microscope and temperature dependence of resistance. Due to the structural similarity of $YBa_2Cu_4O_8$ and YBCO family compounds, this project will compare the electronic properties among a few of the YBCO family superconductors by simulation using the software Quantum Espresso. The relationship between superconductivity and its electronic band structure at normal state will be studied through the simulation. Another aspect of the simulation is Ca-doped $YBa_2Cu_4O_8$. This investigation carried out to better understand the T_c increment in the 10% Ca-doped $YBa_2Cu_4O_8$. In this regard, simulation study including crystal lattice and electronic band structure on the vicinity atoms near the Y/Ca is embarked.

Accordingly, the objectives of this project are:

a) To optimize formation of weigh percentage of $YBa_2Cu_4O_8$ phase by solid state reaction method at ambient pressure.
b) To investigate the effect of different synthesis approach within solid state reaction method on phase formation, lattice structure and T_c of $YBa_2Cu_4O_8$.
c) To study the electronic properties of $YBa_2Cu_4O_8$ and its relation to superconducting properties by density functional theory.
d) To compare the lattice parameters, electronic properties of $YBa_2Cu_4O_8$ and other YBCO family compounds.

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1.4 Scope and limitation of the study

This project is divided into two parts. The first part begins with the synthesis of $YBa_2Cu_4O_8$ using different approach by solid state reaction method. The preparation approaches are (1) Synthesis of $YBa_2Cu_4O_8$ by nitrate precursors, (2) Synthesis of $YBa_2Cu_4O_8$ by tetragonal-$YBa_2Cu_3O_6$ and CuO, and (3) Synthesis of $YBa_2Cu_4O_8$ by $YBa_2Cu_3O_{7-\delta}$ and CuO. Due to unavailability of high gas pressure furnace in Universiti Putra Malaysia, all the heat treatment was conducted at 1 atm. This method of synthesizing samples at 1 atm is more cost effective without relying on expensive high pressure sintering equipment and practical from the point of view of large scale applications. Evolution of the $YBa_2Cu_4O_8$ phase and formation of impurity phases will then be investigated using X-ray diffraction (XRD) technique. The same technique will be used to identify the crystal structure of $YBa_2Cu_4O_8$. Scanning electron microscope will be used for morphology study. Electrical properties of the samples were measured using the four-point probe technique. Thermogravimetric analysis will be performed to check the thermal behaviour of the samples upon subjected to heat treatment. The lattice parameters of $YBa_2Cu_4O_8$ identified in experiment will then be adopted in simulation to analyse the electronic band structure of $YBa_2Cu_4O_8$ by density functional theory using the Quantum Espresso computation package. The first principle calculation including band structure, density of state, Fermi surface, and charge density of $YBa_2Cu_4O_8$ will then be performed. Finally, the simulation results comprising of a series of $YBa_2Cu_3O_7$ compounds, $YBa_2Cu_4O_8$ and Ca-doped $YBa_2Cu_4O_8$ will then be compared and summarized.

1.5 Organization of thesis

Chapter 1 starts with a general introduction of superconductivity including a brief background of superconductor and its applications. Problem statement and objectives as well as scope and limitation of the study are presented.

Chapter 2 provides literature review of the area of study. First of all, this chapter introduces the cuprate superconductors, then background of $YBa_2Cu_4O_8$ including the synthesis processes. It is then followed by ordered reviews of the effects of various doping and particle additions into $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$. Chapter 2 also covers some reviews on the transport properties of the cuprate superconductors. Lastly, review on first principle calculation on YBCO is given.

Chapter 3 describes the sample preparation processes as well as the key equipment including four points probe, thermogravimetric analyser, X-ray diffractometer, and scanning electron microscope. Due to the similarity in the structure of $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_7$, a highlight is given to differentiate these two compounds from the XRD patterns. Finally, the methods and principles used in the simulation works are described.

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Chapter 4 presents the results and discussion for the $YBa_2Cu_4O_8$. In the first section, $YBa_2Cu_4O_8$ samples were prepared using nitrate precursors by conventional solid state reaction method with $NaNO_3$ as an enhancer. The results obtained is then summarized and used to infer the improvement for the sample preparation in the following sections. Successively, starting powers tetragonal-Y123 and CuO were used to prepare Y124. However, the results indicate that getting tetragonal-Y123 first is an unnecessary step, thus, Y124 was instead prepared directly from starting powders Y123 and CuO. All results from different preparing procedures are then summarized and related insights are given.

Chapter 5 presents the simulation works based on density functional theory. The simulation results on crystal lattice and of $YBa_2Cu_4O_8$ and the YBCO family compounds are first addressed and then followed by the electronic band structure analysis of the compounds. Results of Ca-doped $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_7$ are then elaborated and explained.

Chapter 6 concludes the thesis based on the results obtained in this project and future works are proposed.

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LIST OF PUBLICATIONS

C.M. Cheong, et al.; ***Charge Distribution in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ by Density Functional Theory***; Materials Science Forum, Vol. 846, pp. 561-566, 2016.

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