1990

Effect of CO₂ on the Processing of Y-Ba-Cu-O Superconductors

Cunzheng Zhang
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Zhang, Cunzheng, "Effect of CO₂ on the Processing of Y-Ba-Cu-O Superconductors" (1990). *Master's Theses*. 82.

DOI: <https://doi.org/10.31979/etd.u2fm-m7np>
https://scholarworks.sjsu.edu/etd_theses/82

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1342744

Effect of CO₂ on the processing of Y-Ba-Cu-O superconductors

Zhang, Cunzheng, M.S.

San Jose State University, 1990

Copyright ©1991 by Zhang, Cunzheng. All rights reserved.

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

NOTE TO USERS

**THE ORIGINAL DOCUMENT RECEIVED BY U.M.I. CONTAINED PAGES WITH
PHOTOGRAPHS WHICH MAY NOT REPRODUCE PROPERLY.**

THIS REPRODUCTION IS THE BEST AVAILABLE COPY.

**EFFECT OF CO₂ ON THE PROCESSING OF Y-Ba-Cu-O
SUPERCONDUCTORS**

A Thesis

Presented to

**The Faculty of the Department of Materials Engineering
SAN JOSE STATE UNIVERSITY**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

By

Cunzheng Zhang

December, 1990

APPROVED FOR THE DEPARTMENT OF
MATERIALS ENGINEERING

Guna Selvaduray
Dr. Guna Selvaduray

U. Balachandran
Dr. U. Balachandran

K. S. Sree Harsha
Dr. K. S. Sree Harsha

APPROVED FOR THE UNIVERSITY

Serena H. Stanford

ABSTRACT

EFFECT OF CO₂ ON THE PROCESSING ON Y-Ba-Cu-O SUPERCONDUCTORS

by Cunzheng Zhang

The superconducting properties of YBa₂Cu₃O_{6+x} reacted with various known ratios of O₂/CO₂ gas mixtures during sintering at different temperatures was studied. J_c was found to decrease drastically upon reaction with CO₂, becoming zero at certain CO₂ activities. The stability region for the 123 superconductor, as a function of CO₂ activity and temperature, was empirically formulated as follows:

$$\log p_{\text{CO}_2} = (-45,000)/T + 33.4$$

The grain boundaries in sintered samples with J_c = 0 was investigated with HRTEM in conjunction with EDS. Two distinct types of grain boundaries were observed. Approximately 10% of the grain boundaries were wet by a thin layer of a second phase, deduced to be BaCuO₂. The remaining boundaries were sharp grain boundaries. The grain structure near the sharp grain boundaries were tetragonal. These two types of grain boundaries are thought to be responsible for J_c being zero.

ACKNOWLEDGEMENTS

The author wishes to express her heartfelt thanks to Dr. Guna Selvaduray, Associate Professor, San Jose State University, and Dr. U. Balachandran, Argonne National Laboratory, for their advice and leadership throughout this work. The author also appreciates the valuable input and critique from Dr. K. S. Sree Harsha, her Thesis Reading Committee Chairperson.

The author wishes to acknowledge the assistance of several members of Argonne National Laboratory. Special thanks are extended to: S. Dorris, W. Wu, M. Lanagan for instruction on use of the scanning electron microscope, optical microscope and X-ray diffractometer; J. Emerson for setting up the furnaces used; A. Youngdahl, H. Shi, D. Shi for helping on superconducting properties measurements; and A. Philippides, Y. Li, Y. Gao, J. Chen and Cha-Yang Chu for assistance in use of the transmission electron microscope. Thanks also to K. Goretta for much counsel and R. Poeppel for his support of this project.

This work was supported by the U. S. Dept. of Energy, Offices of Energy Storage and Distribution, Conservation and Renewable Energy, and Basic Energy Sciences-Materials Science under contract W-31-109-ENG-38. The program was administered through the Argonne Division of Educational Programs.

C.Z.

TABLE OF CONTENTS

Chapter		page
ABSTRACT		iii
ACKNOWLEDGMENTS		iv
TABLE OF CONTENTS		v
LIST OF ABBREVIATIONS		viii
LIST OF TABLES		ix
LIST OF FIGURES		x
1. INTRODUCTION		1
1.1. The History Of Superconductivity		1
1.2. The Basic Properties Of Superconductors		5
2. AN OVERVIEW OF $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ SUPERCONDUCTOR		9
2.1. Structure Of 123 Compounds		9
2.2. The Critical Current Density In 123 Compounds		15
2.3. The Processing Of 123		17
2.3.1. Calcination		18
2.3.2. Sintering		24
2.3.3. Annealing		30
2.4. The Problems In 123		31
3. THE PURPOSE AND AIM OF EXPERIMENT		34
3.1. Experimental Approach		35
4. EXPERIMENTAL METHODOLOGY		38
4.1. Synthesis Of Phase-Pure 123 Powders		38
4.1.1. Raw Materials		38

4.1.2.	Preparation of 123 Powders	38
4.1.3.	Phase Composition Studied By DTA and XRD	44
4.2.	Sintering And Annealing	48
4.3.	Testing	49
4.3.1.	Density and J_c Measurement	49
4.3.2.	T_c Measurement	49
4.3.3.	Microstructure	51
4.3.4.	XRD Measurement	51
4.4.	Reannealing	51
5.	EXPERIMENTAL RESULTS	53
5.1.	Effect Of Sintering Temperature And Atmosphere On Density And J_c	53
5.1.1.	Sintering Temperature	53
5.1.2.	Atmosphere	53
5.2.	Microstructure	58
5.3.	The Relationship Between T_c And Atmosphere	62
5.4.	Microstructure And Composition Determined By TEM	67
5.5.	Composition Determined By XRD	75
5.6.	Reannealing	78
6.	DISCUSSION	80
6.1.	Effect Of CO_2	80
6.1.1.	Effect of Lower CO_2 Content (<0.5)	80
6.1.2.	Reaction with Higher CO_2 Content (=5%)	87
6.2.	Effect Of Sintering Temperature	88
6.3.	Reaction At Different Temperatures	89
6.4.	Diffusion Of CO_2	91
7.	CONCLUSIONS	93
	REFERENCES	95

BIBLIOGRAPHY	103
APPENDIX A. Summary of the Characteristics of Type I and Type II Superconductors	104
APPENDIX B. Calculation of Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Partial Pressure of CO_2	105
APPENDIX C. Calculation of Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Partial Pressure of O_2	106
APPENDIX D. The Average Weight and Volume of the Samples	107
APPENDIX E. Effect of Sintering Temperature on the Densities and J_c Values	108

LIST OF ABBREVIATIONS

123	$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$
211	Y_2BaCuO_5
011	BaCuO_2
001	CuO
DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectroscopy
H_c	Critical Magnetic Field
HRTEM	High-Resolution Transmission Electron Microscopy
J_c	Critical Current Density
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion-Mass Spectroscopy
T_c	Critical Temperature
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction

LIST OF TABLES

Table	Page
1. Superconductivity Records Through the Years -----	5
2. Phases Present When $\text{YBa}_2\text{Cu}_3\text{O}_7$ is Heated to 1000°C and Cooled in the Indicated Atmosphere -----	24
3. Liquidus Temperature in Y-Ba-Cu-O System -----	29
4. Sintering and Annealing (450°C) Schedules of 123 Sample in CO_2/O_2 (Ambient Pressure) Gas Mixtures -----	37
5. The Calcining Conditions of the Prepared Powders -----	41
6. Impurity Phases in 123 Powders from Different Calcining Conditions -----	47
7. X-Ray Diffraction for the Samples Sintered in $5\% \text{CO}_2 + \text{O}_2$ -----	78

LIST OF FIGURES

Figure	Page
1. The Critical Surface of Superconducting States -----	8
2. Structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ -----	10
3. Detail of the Oxygen-atom Ordering in the $z = 0$ Plane of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ -----	11
4. Oxygen Content Dependence of the Resistive Superconducting Transition Temperature in $\text{YBa}_2\text{Cu}_3\text{O}_x$ for $6.3 < x < 7$ -----	14
5. Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Carbonate Formation ($p_{\text{O}_2} = 1 \text{ atm}$) -----	21
6. (a) BaO-CuO- Y_2O_3 ternary phase diagram (b) Schematic of Binary Cut of Fig.6(a) -----	26
7. Ternary Phase Diagram of the Liquidus Surface in the System $\text{YO}_{1.5}$ - BaO - CuO in Equilibrium with Air -----	28
8. Time – Temperature – Transformation Diagram for the Superconductivity Transition of a Typical 123 Compound - -	32
9. Flow Chart Showing the Experimental Schedule -----	39
10. XRD Patterns of Y_2O_3 , BaCO_3 and CuO Powders -----	40
11. Schedule for Calcination of 123 Powders at 900°C Maximum Temperature ($p_{\text{O}_2} = 2 \text{ mm Hg}$) -----	42
12. Particle Size Distribution of Calcined 123 Powders -----	43
13. DTA Traces of Samples -----	45
14. XRD Patterns of Calcined Powders of 123 -----	46

15. The Effect of Sintering Temperature on Density -----	54
16. The Effect of Sintering Temperature on J_c -----	55
17. Stability of 123 Compounds as a Function of p_{CO_2} and Temperature -----	57
18. Optical Micrographs for Samples Sintered under 100% O_2 -	59
19. SEM Micrographs of the Fracture Surface for Samples Sintered under 100% O_2 -----	60
20. Grain Size of Samples Sintered under 100% O_2 -----	61
21. Optical Micrographs for Samples Sintered at 1000°C -----	63
22. Resistivity vs Temperature for Samples Sintered at 940°C -----	64
23. RF Susceptibility vs Temperature for Samples Sintered at 940°C -----	65
24. Sample Sintered at 970°C in 0.5% $CO_2 + O_2$ TEM micrograph of a grain boundary -----	68
25. EDS Spectrum Obtained from a Point in the Grain Boundary of a Sample Sintered in 0.5% $CO_2 + O_2$ -----	69
26. Sample Sintered at 970°C in 0.5% $CO_2 + O_2$ HRTEM image of a grain boundary -----	71
27. TEM micrograph for the sample sintered in 0.5% $CO_2 + O_2$ -	73
28. HRTEM image of a grain boundary in the sample sintered in 50 ppm $CO_2 + O_2$ -----	74
29. TEM Micrograph for the Sample Sintered in 5% $CO_2 + O_2$ ---	76
30. XRD Patterns of Decomposed Phases -----	77

31. Section Through the Ternary Phase Diagram Along the Join $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ – Y_2BaCuO_5	81
--	----

1. INTRODUCTION

The property of zero electrical resistance is that which comes immediately to mind in thinking of superconductors. What are superconductors?

Superconductors are materials that exhibit zero electrical resistivity and pronounce diamagnetic properties at extremely low temperatures. They have a number of unique characteristics, but their most notable property and the origin of their name lies in their ability to conduct electrical current with practically no loss of energy.

1.1. The History Of Superconductivity

Soon after Kammerlingh Onnes liquefied helium in 1908, a range of temperatures below 4.2 K became accessible for experiment. In 1911, Onnes investigated the temperature variation of the electrical resistance of mercury in this range. The rather surprising result was the total disappearance of resistance at a critical temperature of 4.15 K. Onnes was taken aback and examined his results and experiments repeatedly. He labelled the new phenomenon superconductivity.⁽¹⁾ The temperature at which a material enters the superconducting state was called the transition temperature or critical temperature, T_c .

A considerable amount of time passed before physicists became aware of the the second distinguishing characteristic of a superconductor, namely, its perfect diamagnetism. In 1933 Meissner found that when a superconductor was cooled below its transition temperature in a magnetic field, H , it excluded the magnetic flux. This phenomenon is known as the Meissner effect.⁽¹⁾ Superconductivity can be destroyed by the application of a magnetic field. If a strong enough magnetic field, called the critical magnetic field, H_c , is applied to a superconducting material, it recovers its normal resistivity.

The report of the Meissner effect stimulated F. London and H. London to propose their equation. This equation numerically explained the Meissner effect and in addition predicted a penetration depth, Λ , for how far a static external magnetic flux can penetrate into a superconductor.⁽²⁾ Following the work of F. and H. London, in 1957 J. Bardeen,^(B) L. Cooper,^(C) and J. R. Schrieffer^(S) presented a theoretical understanding of the nature of superconductivity called the BCS microscopic theory.⁽³⁾ This theory explained the formation of bound electron pairs that carry the supercurrent, and energy gap that stabilizes the superconductive state.

Quite independently of Bardeen, Cooper and Schrieffer, another important event in the history of superconductivity took

place in 1961. Kunzler performed extensive tests on an alloy of tin and niobium (Nb_3Sn) which was discovered by T. Matthias in 1954 and found that Nb_3Sn not only had a high transition temperature, but that it also sustained superconductivity to very high current densities and very high magnetic fields.⁽⁴⁾ This discovery revealed that there are two type of superconductors, Type I and Type II. Type I superconductors exhibit a single critical magnetic field, H_c . Below H_c they exhibit zero resistivity. Type II superconductors behave like Type I materials for fields below a critical level H_{c1} . When fields are increased above H_{c1} , however, Type II materials allow bulk penetration of magnetic flux. This penetration continues until the magnetic field is increased above the upper critical level, H_{c2} . This region where $H_{c1} < H < H_{c2}$ is a mixed state; however, Type II materials still act as superconductors. Since the superconductor's energy is not utilized in expelling flux, Type II superconductors can remain superconducting in far greater magnetic fields than Type I superconductors. Materials with high critical temperatures tend to fall in the Type II category. Nb_3Sn and many other intermetallic compounds and alloys are characteristic of Type II superconductivity. The characteristics of Type I and Type II superconductivity are summarized in Appendix A.

The modern age of the so-called high- T_c superconductors began in April 1986, when Muller and Bednorz⁽⁵⁾ synthesized a compound containing four elements and found superconductivity at

the lofty temperature of 35 K. This reached a new era in superconductivity. By December 1986 the results of Muller and Bednorz had been duplicated and confirmed by groups at the University of Tokyo,⁽⁶⁾ the Chinese Academy of Sciences in Beijing,⁽⁷⁾ and by Ching-Wu Chu and his colleagues at the University of Houston.⁽⁸⁾ Many other laboratories joined the hunt for new higher-temperature ceramic oxide superconductors. Critical temperatures up to 52 K were eventually achieved. In March 1987, Wu and his colleagues broke the liquid-nitrogen barrier with yttrium-barium-copper oxide.⁽⁹⁾ This ceramic becomes superconducting at an astonishing temperature above 90 K. This critical temperature is much higher than the boiling point of nitrogen, which is 77 K. In January and February of 1988 the BiSrCaCuO⁽¹⁰⁾ and TiBaCaCuO^(11,12) systems with transition temperature in the 110-120 K range were reported. Table 1⁽¹³⁾ shows the history of major improvements in superconductivity and reflects how ceramics revolutionized this area.

Table 1. Developmental History of Superconductivity

Material	Type	$T_c(K)$	Year of Discovery
Hg	Element	4.1	1911
Pb	Element	7.2	1913
Nb	Element	9.3	1930
Nb ₃ Sn	Intermetallic	18.1	1954
Nb ₃ (Al _{0.75} Ge _{0.25})	Intermetallic	20-21	1966
Nb ₃ Ga	Intermetallic	20.3	1971
Nb ₃ Ge	Intermetallic	23.2	1973
Ba _x La _{5-x} Cu ₅ O _{5(3-y)}	Ceramic	30-35	1986
(La _{0.9} Ba _{0.1}) ₂ CuO _{4-δ} , at 1 GPa	Ceramic	52.5	1986
YBa ₂ Cu ₃ O _{7-δ}	Ceramic	90-95	1987
BiSrCaCuO	Ceramic	105-120	1988
TlBaCaCuO	Ceramic	110-125	1988

1.2. The Basic Properties Of Superconductors

Superconductivity is produced by a supercurrent flow which is comprised of electron pairs, as opposed to the flow of individual electrons in the normal metallic state.

In general, the resistivity of a metal may be written as:

$$\rho = \frac{m}{ne^2\tau} \quad (\text{Eq.1})$$

where m is the mass of electron, τ is the collision time. Since temperature decreases and therefore τ increases, this equation points out that ρ decreases as the temperature is lowered. As T decreases, the lattice vibrations begin to "freeze," and hence the scattering of the electrons diminishes. This results in a longer τ and hence a smaller ρ , as indicated by the above equation. If τ becomes infinite at sufficiently low temperatures, then the resistivity vanishes entirely. But superconductivity is a special phenomenon. The current transport in the superconducting state is a mixture of paired electrons that comprise the "supercurrent" and unpaired electrons that behave very much in the normal fashion. At nonzero temperatures, not all conduction electrons participate in the superconducting behavior. However, as a superconductor is cooled below T_c , ordinary electrons "condense" into superconducting pairs. These pairs consist of electrons with opposite spins and equal momenta so that the net momentum and the net spin of the pair are zero.⁽¹⁴⁾ It is these electrons which are responsible for superconductivity.

Superconductivity also exists up to a maximum magnetic field strength. The critical magnetic field strength H_c , when exceeded, will destroy superconductivity. The magnetic field may be applied externally or may be a "self-field," i.e., one that arises from an electrical current passing through the superconductor

itself. The current a superconductor can sustain in the superconducting state is its critical current density, J_c . Therefore superconductivity occurs within a surface passing through T_c , H_c and J_c , as shown in Figure 1.⁽¹⁵⁾ Outside this surface the superconductor reverts to its normal state of electrical resistance.

Figure 1. The Critical Surface of Superconducting States (Ref. 15)

2. AN OVERVIEW OF $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ SUPERCONDUCTORS

A little more than one year after Bednorz and Muller showed the existence of superconductivity in copper containing oxides, several copper oxide systems were shown to have the ability to be superconducting at temperatures above 90 K.⁽¹⁰⁻¹²⁾ Among these superconducting materials, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds, commonly known as "123" compounds, have received considerable attention because of their high T_c and high H_c .^(16,17) In this chapter past research on 123 compounds is briefly reviewed.

2.1. Structure Of 123 Compounds

The structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is closely related to that of perovskite,^(18,19) with oxygen concentrations in the range of $0 \leq x \leq 1$.^(20,21) According to the overall oxygen stoichiometry and the ordering of oxygen vacancies, the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ exists in two forms: orthorhombic and tetragonal.⁽¹⁹⁾

Figures 2 and 3 show the structure of the 123 unit cell, as presented by Jorgensen et al..⁽²¹⁾ As can be seen from Figure 2, in the orthorhombic structure the $(0, 1/2, 0)$ and $(1/2, 0, 0)$ sites are crystallographically inequivalent, and the oxygen atoms are fully ordered onto the $(0, 1/2, 0)$ site at room temperature, thus resulting in the one-dimensional CuO_3 chains parallel to the b axis. Along the c -direction, it can be represented as $\text{CuV}_o\text{-BaO- CuO}_2$,

Figure 2. Structure of YBa₂Cu₃O_{6+x}. (a) The orthorhombic Pmmm phase; (b) The tetragonal P4/mmm phase (Ref. 21)

Figure 3. Detail of the Oxygen-atom Ordering in the $z = 0$ Plane of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$: (a) Orthorhombic phase exhibiting complete ordering of oxygen atoms onto the $(0, 1/2, 0)$ site which results in one-dimensional CuO_3 chains along the b axis; and (b) Tetragonal phase showing a disordering of the oxygen atoms in the same plane (Ref. 21)

where V_o represents oxygen vacancies, as shown in Figure 2(a). The structure has orthorhombic symmetry. The orthorhombic $YBa_2Cu_3O_{6+x}$ structure has a space group of Pmmm. Its lattice constants are $a = 3.82 \text{ \AA}$, $b = 3.89 \text{ \AA}$, $c = 11.68 \text{ \AA}$.

In the tetragonal structure, as shown in Figure 2(b), the oxygen sites at $(1/2, 0, 0)$ and $(0, 1/2, 0)$ are symmetrically equivalent. The disordering of the oxygen atoms are in a two-dimensional layered structure where the layers attain a nearly octahedral Cu-O configuration consisting of a partially occupied ($< 25\%$), nearly square-planar, Cu-O network perpendicular to the c axis. The tetragonal structure, which is stable above 650°C , has a space group of P4/mmm. Its lattice constants are $a = b = 3.92 \text{ \AA}$, $c = 11.94 \text{ \AA}$.

The transition from the orthorhombic phase to the tetragonal phase is an order-disorder transition which occurs at an oxygen stoichiometry of 6.5, presumably going from orthorhombic at $0.5 < x < 1$ to tetragonal at $0.0 < x < 0.5$.^(21,22) It is thought that this change is accompanied by a dramatic shift of the oxygen atoms into the normally vacant sites which destroys the normal one-dimensional Cu-O chains of the orthorhombic structure and results in a highly disordered two-dimensional Cu-O network of the tetragonal structure.

The transition of the orthorhombic phase to the tetragonal phase could have a large effect on the electronic structure of the compound.⁽²³⁾ Although several detailed aspects of this phase transition remain unexplored, it is clear that the superconducting properties of 123 compounds are strongly affected by their oxygen content.⁽²²⁻²⁴⁾ For $x \sim 1$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is in the orthorhombic phase and exhibits superconductivity at 90 K. As the oxygen content decreases, at $0.6 < x < 0.7$, the transition temperature of the orthorhombic phase decreases to 60 K. At $x \sim 0.4$, the material enters the tetragonal phase and superconductivity is destroyed. This is shown in Figure 4.

It is thought^(18,25) that the decrease in the superconducting transition temperature is due to a disordering of the oxygen chains. In the 90 K superconducting phase, the oxygen atoms in Cu-O chains are fully ordered, whereas in the 60 K superconducting phase, the oxygen atoms and vacancies in the Cu-O chains are only partially ordered. At an oxygen stoichiometry below 6.5, there are no stable oxygen ordering states. The oxygen concentration affects the spatial arrangement of oxygen chain. The spatial arrangement of oxygen atoms affects the average charge of Cu-O plane which determines the superconducting transition temperature.

The $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor, with a transition temperature of 90 K, shows it to possess (110) reflection twinning.⁽²⁶⁾

Figure 4. Oxygen Content Dependence of the Resistive Superconducting Transition Temperature in $\text{YBa}_2\text{Cu}_3\text{O}_x$ for $6.3 < x < 7$ (Ref. 20)

However, the tetragonal material is untwinned. So when the orthorhombic structure reverts back to tetragonal the twinning disappears.⁽²⁷⁾

2.2. The Critical Current Density In 123 Compounds

One of the early concerns was whether the new 123 superconductor would be capable of carrying a large current. The critical current density in the ceramic superconductors can be potentially as high as 10^8 A/cm², the limit being set by optimum pinning of the magnetic flux.⁽²⁸⁾ The pinning of the magnetic flux can increase the critical current density, since the motion of fluxons will result in dissipation of normal currents.⁽²⁹⁾ However, present critical currents are far below this, particularly for sintered ceramic materials.⁽³⁰⁾ The sintering method yields a coarse, granular polycrystalline material whose current-carrying ability is severely limited by weak links at the grain boundaries.⁽³¹⁾ A common form of the weak link consists of a very thin insulating layer between two larger volumes of superconductor. The layer, rather than the bulk material, will now control the current density. For sintered powders the critical current density, J_c , is less than 10^3 A/cm² even when the applied magnetic field is zero ($H = 0$).⁽³⁰⁾ Thus the weak-links of the grain boundaries have been the subject of considerable research. Much effort has been concentrated on characterizing grain boundaries. The composition at grain boundaries in sintered 123 has been

investigated by several groups. Babcock et al.⁽³²⁾ reported that the boundaries of 123 are somewhat copper-rich and barium-and oxygen-deficient. Also, some microcracks⁽³³⁾ and amorphous thin layers⁽³⁴⁾ have been found near the grain boundaries. Kogure⁽³⁵⁾ reported that a new phase, $\text{YBa}_2\text{Cu}_4\text{O}_x$, referred as "124," is often observed at boundaries between grains. The effect of the 124 phase at grain boundaries must be considered as having an influence on J_c , though the existence of the 124 phase at the grain boundaries is not the main reason for the transport currents being lower by several orders of magnitude. Dimos et al.⁽³⁶⁾ reported the dependence of J_c across grain boundaries on the misorientation angle between 123 bicrystals, suggesting that grain boundaries are intrinsically weak links in these materials. Intergranular weak links are also expected because of anisotropic conductivities and poor mechanical connectivity. Besides the random orientation in polycrystalline materials, there are probably other potential reasons for weak links at grain boundaries. It is speculated that 1 or 2 monolayers of carbon exist at the grain boundaries.⁽³⁵⁾ All of this means that there exist grain boundaries where the composition is somewhat different from that in the bulk. These abnormalities at grain boundaries are generally dependent on material fabrication conditions.⁽³⁷⁾ Microstructural improvements such as increased density and reduction of second phases at grain boundaries can therefore be expected to increase the J_c value.

There is another factor causing low J_c : the high anisotropy of the orthorhombic lattice with respect to current flow. This results in critical currents in the Cu-O plane being an order of magnitude greater than that in the *c*-direction, as mentioned in Section 2.1. This problem can be greatly reduced by orienting or texturing the grains, so that the *c*-direction is perpendicular to the transport current flow direction, either with a magnetic field,⁽³⁸⁾ or by melting and regrowing the solid in the presence of a temperature gradient. This is normally referred to as melt-texturing.⁽³⁹⁾

2.3. The Processing Of 123

As discussed in Sections 2.1 and 2.2, due to the anisotropy in the superconducting properties and the existence of composition inhomogeneities at the grain boundaries in bulk materials, special attention must be given during the processing of ceramic superconductors. In general, the processing goal is to obtain a uniform fine grained material in order to obtain the best mechanical and superconducting properties.

The most common processing method used to prepare the 123 superconductor can be divided into three steps: mixing, calcining and sintering.

The first step is synthesis of the superconducting powders. This may be done by several aqueous techniques, such as the liquid-mix technique,⁽⁴⁰⁾ sol-gel processing,^(41,42) or chemical precipitation.^(43,44) These techniques in principle appear to be more advantageous than grinding; in practice their full potential has yet to be realized.

Another popular method of synthesis is by solid-state reaction. Producing a superconductor in this way is the simplest method. The starting powders are mechanically mixed and then calcined. This produces high quality materials if sufficient care is employed.⁽⁴⁵⁾ This project employs solid-state reaction for synthesis of 123 compounds.

2.3.1. Calcination

The thermal processing of the precursor material into $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ superconductors is an extremely crucial step. It depends on balancing a number of reaction rates. Usually the Y_2O_3 , BaCO_3 and CuO powders are used as starting materials. After mechanically mixing, these powders are calcined. It is reported⁽⁴⁶⁾ that during calcination, as the temperature increases, the following reactions take place:

These equilibria imply that the calcination atmosphere significantly influences the resulting products. Since BaCO_3 is used, CO_2 is released during calcination. The concentration of CO_2 can quickly reach its equilibrium value, and stagnant regions of CO_2 can form, even in systems with flowing gas. This CO_2 pressure, depending on the temperature and other thermodynamic conditions, may cause other decomposition reactions, thereby forming undesired phases. All these decomposition phases significantly reduce the critical current density of 123.

The relationship between $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, O_2 and CO_2 has been investigated by Fjellvåg et al.⁽⁴⁷⁾ It may be understood by reactions (4) and (5), which are carried out at a total pressure of 1 atm, i.e. 0.999 atm O_2 and 0.001 atm CO_2 . Below $730 \pm 10^\circ\text{C}$ the oxides of yttrium and copper are formed, together with barium carbonate, according to the following reaction:

Above $730 \pm 10^\circ\text{C}$ $\text{Y}_2\text{Cu}_2\text{O}_5$, in addition to barium carbonate and copper oxide, are reaction products, according to the following reaction:

As can be seen from reactions (4) and (5), the partial pressure of CO_2 will determine the extent to which the non-superconducting reaction products are formed. The effect of CO_2 partial pressure on the oxide-carbonate equilibrium, as a function of temperature, is shown in Figure 5.⁽⁴⁸⁾ The bold line represents the effect of CO_2 partial pressure, as a function of temperature, on $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. This can be represented analytically by the following equation:

$$\log p_{\text{CO}_2} = -\frac{8900}{T} + 5.7 \quad (\text{Eq. 6})$$

where p_{CO_2} is in atmospheres and the temperature T is above 730°C .

At CO_2 partial pressures to the "north east" of the bold line in Figure 5, the 123 compound will decompose according to reaction (5). At 900°C , the threshold partial pressure of CO_2 is 0.02 atm, or 2%. The calculation is shown in Appendix B. For a CO_2 partial pressure of 0.02, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is stable at temperatures below 900°C . Thus in order to calcine the precursor material and obtain a 123 composition, the local CO_2 concentration must be maintained below this value of 2%.

Figure 5. Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Carbonate Formation ($p_{\text{O}_2} = 1$ atm) (Ref. 47)

The oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is a function of both temperature and oxygen partial pressure. From Equations 4 and 5, if the oxygen content is 6.5, (that is $123 = \text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $x = 0.5$) no oxygen is evolved or consumed during the carbonation. Since the transition of the orthorhombic phase to the tetragonal phase occurs at the oxygen content of $x \sim 0.5$, in order to keep of $x > 0.5$, a quantitative treatment of the reactions with CO_2 will require knowledge of the equilibrium between $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and oxygen.

Experiment shows⁽⁴⁷⁾ that the x versus $\frac{1}{T}$ relationship is essentially linear in the temperature range 600-900°C for a constant oxygen partial pressure of 1.00 atm, and can be parameterized as follows:

$$x = A/T + B \quad (\text{Eq. 7})$$

where A and B have values of 1390 K and -0.83 , respectively. The oxygen partial pressure in equilibrium with $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in the temperature interval 520-780°C is empirically described as:⁽⁴⁷⁾

$$\log p_{\text{O}_2} = - C/T + D \quad (\text{Eq. 8})$$

where $C = -8350$ K, $D = 8.0$ for p_{O_2} specified in atm. According to Equation 8, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is stable at 771°C in pure oxygen (1.00 atm) and at 689°C in air. The calculations are shown in Appendix C.

For $x = 7$, Equation 5 can be written as follows:

The standard Gibbs free energy function for this chemical reaction at equilibrium is:

$$\Delta G^\circ = - RT \ln \frac{(p_{O_2})^{1/4}}{(p_{CO_2})^2} \quad (\text{Eq.10})$$

This equation gives the equilibrium p_{CO_2} and p_{O_2} ratio that defines the stability region of $YBa_2Cu_3O_7$ superconductors.

The effect of O_2 , CO_2 and HO_2 partial pressure on the phases present when 123 compounds were heated to 1000°C was investigated by Gallagher et al,⁽⁴⁹⁾ and the results are presented in Table 2.

Table 2. Phases Present When $\text{YBa}_2\text{Cu}_3\text{O}_7$ is Heated to 1000°C and Cooled in the Indicated Atmosphere

Atmosphere	Phases Present
Wet O_2	$\text{YBa}_2\text{Cu}_3\text{O}_7$
Dry O_2	$\text{YBa}_2\text{Cu}_3\text{O}_7$
0.1% CO_2 in O_2	$\text{YBa}_2\text{Cu}_3\text{O}_7$
1% CO_2 in O_2	$\text{YBa}_2\text{Cu}_3\text{O}_7$ with broadened lines
10% CO_2 in O_2	major BaCO_3 , strong $\text{Y}_2\text{Cu}_2\text{O}_5$, CuO
100% wet or dry CO_2	major BaCO_3 , Y_2O_3 , Cu_2O , sl CuO , $\text{Y}_2\text{Cu}_2\text{O}_5$

2.3.2. Sintering

Sintering is the process whereby powders are compacted into useful shapes and heated to form dense, strong material. Sintering of superconducting materials can occur either by solid-state diffusion or by the presence of a liquid phase. In the most idealized form, solid-state sintering, the powder consists of individual crystal grains which remain solid throughout the heat treatment. The system is heated to temperatures where diffusion of the atoms in the solid state can occur. Atom movements can then bring about a reduction in the surface energy of the system either by densification or by grain growth. Since the former process results in a reduction in the particle-particle distance, shrinkage of up to 20% occurs and porosity is removed as required for component fabrication. The rates of these processes are

enhanced by higher sintering temperatures or by finer particle sizes. Densification is further enhanced if pressure can be applied to the system during heating, thus increasing the driving force for shrinkage and pore elimination. However, solid-state sintering is relatively slow, and in the absence of a liquid phase, it is difficult to obtain densities very close to theoretical density. Sintering at high temperature with liquid formation tends to produce dense components, since the liquid phase wets the solid and dissolves it appreciably. The driving force for the densification is the decrease of the interfacial energy between the solid and the liquid. However, the presence of a liquid phase will lead to explosive grain growth. In the case of 123, the liquid phase which usually is nonsuperconducting is incongruent with the superconducting solid phase, and phase separation will thus occur. The liquid phase coats the grain surfaces and give rise to the weak link effect.

In order to appreciate the critical sintering temperature in processing 123 material, it is necessary to understand its phase diagram. There are several different phase equilibria in the Y_2O_3 -BaO-CuO system. The Y_2O_3 -BaO-CuO-O ternary phase diagram for the temperature range of 950-1000°C is shown in Figure 6(a). A section of the phase diagram, from $Ba_2Y_2CuO_5$ to "Z" on the BaO-CuO axis, containing $YBa_2Cu_3O_7$, is shown in Figure 6(b).⁽⁵⁰⁾ The "region of partial melting," in Figure 6(a), includes the ternary eutectic and the composition field when 123 is in equilibrium with melts.

Figure 6. (a) BaO-CuO-Y₂O₃ ternary phase diagram (Ref. 50)
 (b) Schematic of Binary Cut of Fig.6(a) (Ref. 50)

$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ does not melt congruently. As can be seen from Figure 6(b), $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is in equilibrium with melts higher in CuO content than itself. Small compositional variations throughout the 123 material will decrease the melting temperature.

Figure 7 and Table 3 give the invariant temperatures for this system. Of particular significance for sintering of 123 material is the presence of the ternary eutectic, e1, between 123, BaCuO_2 and CuO_x . A liquid phase is formed on heating to the eutectic temperature if the composition falls within the three phase region. If the three phases, 123, YBaCuO_5 and CuO_x , are present and in intimate contact, they will undergo the pseudo-peritectic reaction at the temperature line $e4 \rightarrow p1$ and form a liquid phase at the composition p1. Therefore, small compositional variations can produce pockets of low melting materials which may act to promote liquid phase sintering. The nonsuperconducting liquid phase will coat the superconducting grains, and poor superconducting materials will therefore result.

From Table 3, it is also noticed that the melting temperature of 123 is lower in air than in pure oxygen. This was also confirmed by Chen⁽⁵¹⁾ and Tu⁽⁵²⁾. Their experiments show that as p_{O_2} decreases, the melting point of 123 decreases. If phase-pure 123 is used, the sintering temperature in high oxygen partial pressures

Figure 7. Ternary Phase Diagram of the Liquidus Surface in the System $\text{YO}_{1.5}$ - BaO - CuO_x in Equilibrium with Air (Ref. 48)
 *e1(898°C), e2(902°C), p1(933°C), p2(956°C), m1(999°C)

Table 3. Liquidus Temperature in Y-Ba-Cu-O System (48)

Invariant Point*	Reaction	Reaction Temperature (°C)	
		in air	in O ₂ (1 atm.)
e1	$123 + \text{BaCuO}_2 + \text{CuO} \longleftrightarrow \text{L(e1)}$	898	925
e2	$\text{BaCuO}_2 + \text{CuO} \longleftrightarrow \text{L(e2)}$	902	938
e3	$\text{Y}_2\text{BaCuO}_5 + \text{BaCuO}_2 \longleftrightarrow \text{L(e3)}$		1015
p1	$123 + \text{CuO} \longleftrightarrow \text{Y}_2\text{BaCuO}_5 + \text{L(p1)}$	933	962
p2	$\text{Y}_2\text{BaCuO}_5 + \text{CuO} \longleftrightarrow \text{Y}_2\text{Cu}_2\text{O}_5 + \text{L(p2)}$	956	990
p3	$123 + \text{BaCuO}_2 \longleftrightarrow \text{Y}_2\text{BaCuO}_5 + \text{L(p3)}$		1010
m1	$123 \longleftrightarrow \text{Y}_2\text{BaCuO}_5 + \text{L(m1)}$	999	1028

* The letter "e" stands for eutectics, "p" stands for pseudo-peritectic and "m" stands for peritectic decomposition.

can approach 1000°C. In order to produce high-density 123 without formation of a liquid phase, the sintering temperature, atmosphere and particle size distribution should be carefully considered.

Therefore, in order to achieve a uniform fine grained 123 superconductor, careful control of the calcination and sintering steps must be achieved. During calcination, it is essential to avoid the formation of liquid phases. This limits the temperature and

the CO₂ partial pressure at which calcination may be performed. In sintering, reactive liquid phase sintering and the resulting explosive grain growth must be avoided. This limits the sintering temperature and requires very careful control of particle size and phase composition.

2.3.3. Annealing

Sintering must be followed by an annealing step. 123 loses oxygen at the sintering temperature and forms the tetragonal structure. The decrease of the oxygen content causes simultaneously a lowering of the critical temperature. On the other hand, an annealing step at relatively low temperatures, in an oxidizing atmosphere, can improve the superconducting properties.⁽⁵³⁾ The oxygen content increases according to the following reaction:

Annealing is normally carried out by holding the compounds at approximately 400°C for 2-10 hours.⁽⁵²⁾ The driving force for the tetragonal to orthorhombic transformation is governed by the change of their Gibbs free energy, ΔG , which is proportional to the undercooling, ΔT , and the rate of oxygen diffusion, which is inversely proportional to ΔT . The rate of oxygen diffusion affects the ΔG change for the tetragonal to orthorhombic transformation

because it is oxygen diffusion that controls the localized oxygen partial pressure within the bulk superconductors. A graphical representation for the kinetic process is given in Figure 8, where the contributions of the temperature and time changes to both nucleation and growth of the orthorhombic phase are shown. From Figure 8, it can be seen that the shortest transition time for the tetragonal phase to the 90 K orthorhombic phase transformation occurs at approximately 400°C.

However, some results show this annealing treatment may lead to partial carbonation of the sample, with impurities probably accumulating at grain boundaries and surfaces. This problem can be avoided by using CO₂-free gases.⁽⁴⁷⁾

2.4. The Problems In 123

The major problem with 123 superconductors is the low J_c value in bulk samples. A possible cause of this problem is blockage of the superconducting currents at grain boundaries. It is generally accepted⁽³²⁻³⁶⁾ that a few angstroms thick second phase present the grain boundaries, or simply changes in the stoichiometry at the boundary, could be the source of the problem.

123 compounds are also inherently unstable with respect to atmospheric or condensed moisture.^(55,56) This is due to the large

Figure 8. Time – Temperature – Transformation Diagram for the Superconductivity Transition of a Typical 123 Compound (Ref. 24)

enthalpies of formation of BaCO_3 and Ba(OH)_2 , according to the following reactions:(57)

Ba(OH)_2 can further react with CO_2 to form barium carbonate(57,58):

It is suggested that these second phases, BaCO_3 and Ba(OH)_2 which are insulators, are likely to coat the grain boundaries of 123, thus deleteriously reducing the J_c value.

3. THE PURPOSE AND AIM OF EXPERIMENT

The processing of $\text{YBa}_2\text{Cu}_3\text{O}_7$ material requires protection from ambient water and CO_2 . A detectable reaction between the 123 and CO_2 will proceed even at relatively low CO_2 partial pressures and high temperatures, because of the high basicity of the constituent oxides, in particular BaO.

Depending upon the method by which the 123 powder is calcined there may be residual carbonate/oxyarbonates left in the powder. This residual carbonate decomposes and gives off CO_2 during sintering of samples made from these powders. The CO_2 partial pressure could also cause other decomposition reactions, leading to the formation of second phases on the grain boundaries, thereby decreasing the J_c value.

Another source of CO_2 is the compressed air or oxygen needed during sintering. These gases, which are contained in pressurized cylinders, contain varying amounts of CO_2 . The purpose of this project, therefore, was to study the effect of CO_2 containing atmospheres on the sintering characteristics and final product characteristics.

The equilibrium constant for Reaction (9), which is the reaction between 123 compounds and CO₂, can be determined from Equation 10, which is repeated here:

$$\Delta G^\circ = -RT \ln \frac{(p_{O_2})^{1/4}}{(p_{CO_2})^2} \quad (\text{Eq.10})$$

If p_{O₂} is kept close to 1.00 atm, Equation 10 can be written as follows:

$$\begin{aligned} \Delta G^\circ/T &= -2.303R \log(p_{CO_2})^{-2} \\ &= 4.606R \log p_{CO_2} \end{aligned} \quad (\text{Eq.15})$$

Thus plots of log p_{CO₂} versus 1/T can establish the stability region(s) of 123. The line plot of log p_{CO₂} versus 1/T represents an equilibrium value of p_{CO₂} for the corresponding temperature.

3.1. Experimental Approach

In order to investigate the extent to which 123 compounds interact with CO₂, it is desirable to start with phase-pure 123 materials, which can be formed by calcination in air, with rapid heating at 2000°C/h, to 900°C and held for 12 hours.⁽⁵⁹⁾ Four repeated calcinations are required. Fast heating is thought to minimize formation of liquid phases. A calcination temperature of 950°C, at a fast heat-up rate, also appears to be crucial to success.⁽⁶⁰⁾ But such a calcination temperature leads to the

powder being relatively coarse and difficult to fabricate into good, dense, free-flowing ceramics. Also, heating up to 950°C probably produces BaCuO₂ a liquid-phase, as previously mentioned: CuO and 123 can form a molten phase at about 925°C in 1 atm oxygen.⁽⁴⁸⁾

In the present study, the precursor powder was calcined in reduced total pressure (2mm Hg) with oxygen gas flow to keep the partial pressure of CO₂ below the equilibrium value required for the decomposition of 123. The equilibrium value of p_{CO_2} at 900°C is 0.02 atm, and was determined according to the calculations contained in Appendix B. Vacuum calcination is an acceptable method to eliminate the repeated calcinations otherwise needed. The vacuum calcined material was characterized by X-Ray Diffraction (XRD) and Differential Thermal Analysis (DTA) to confirm that the product consisted of phase-pure powders.

After obtaining phase-pure 123 powders, these powders were reacted with O₂/CO₂ gas mixtures, with various known amounts of CO₂, at different temperatures. The sintering conditions used are outlined in Table 4.

Table 4. Sintering and Annealing (450°C) Schedules of 123
Samples in CO₂/O₂ (Ambient Pressure) Gas Mixtures

CO ₂ /O ₂ gas ratio	Sintering Temperature (°C)			
	1000	970	940	910
50 ppm CO ₂	*	*	*	*
500 ppm CO ₂	*	*	*	*
0.5% CO ₂	*	*	*	*
5% CO ₂	*	*	*	*

The phase structure of the samples sintered under varying temperature and CO₂ partial pressure was studied by XRD. This was done in order to monitor the phase decomposition.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the microstructure and second phase formation.

J_c and T_c were measured. The stability region of 123 superconductors as a function of CO₂ partial pressures and temperature was established.

4. EXPERIMENTAL METHODOLOGY

The experimental procedure followed in this investigation is summarized in the flow chart in Figure 9, and is described in this chapter.

4.1. Synthesis Of Phase-Pure 123 Powders

4.1.1. Raw Materials

The raw materials Y_2O_3 , $BaCO_3$ and CuO of purity better than 99.9% were purchased from Rhone-Poulenc. The pure oxygen gas was supplied by Air Products and Chemicals, Inc.. The CO_2/O_2 gas mixtures, with predetermined amounts of O_2 and CO_2 , were supplied by Matheson Gas, Inc..

4.1.2. Preparation of 123 powders

The ternary oxides are prepared from Y_2O_3 , $BaCO_3$ and CuO powders. Required amounts were weighed and mixed by wet ball milling in a polypropylene bottle for 18 hours, using ZrO_2 media and methanol. For 120 g of powders, 75 ml methanol was added. The powders were pan dried, and then sized with a No. 60 sieve. These as-sieved powders were checked by XRD to ensure the mixture consisted of only Y_2O_3 , $BaCO_3$ and CuO powders. Figure 10 shows the XRD pattern of a typical powder. These powders were then calcined. The calcining conditions and schedules are shown in Table 5 and Figure 11, respectively.

Figure 9. Flow Chart Showing the Experimental Schedule

Figure 10. XRD Patterns of Y_2O_3 , BaCO_3 and CuO Powders
(Y = Y_2O_3 , B = BaCO_3 and C = CuO)

Table 5. The Calcining Conditions of the Prepared Powders

Sample No.	Calcining Atmosphere	Calcining Temperature (°C)	Number of Calcination
CZ - A	In Vacuum*	900	2
CZ - B	In Vacuum*	900	1
CZ - C	In Vacuum*	850	2
CZ - D	In Vacuum*	850	1
CZ - E	In Vacuum*	800	2
CZ - F	In Vacuum*	800	1
CZ - G	In Air	900	2
CZ - H	In Air	900	1

* With 2 mm Hg pressure in flowing oxygen

After calcination, these powders were ground using a mortar and pestle and sieved through a No. 400 sieve. Further grinding was done by Centrifugal Milling, using a Type ZM1, Brinkmann Instruments Co. centrifugal milling. (Centrifugal milling involves feeding the powder into a high-speed rotor which shears and crushes the powder, forcing it through a selected screen. The final screen apertures used here were 0.08 millimeter). Particle size analysis of the milled powders was conducted using a Leeds & Northrup Instruments, Model 7995-93, Microtrac Particle Size

Figure 11. Schedule for Calcination of 123 Powders at 900°C
Maximum Temperature ($p_{O_2} = 2$ mmHg)

Figure 12. Particle Size Distribution of Calcined 123 Powders.
 Before centrifugal milling (median particle size = 5.2 μm) and
 after centrifugal milling (median particle size = 2.8 μm)

Analyzer. Figure 12 shows the particle size analysis results of the powder.

4.1.3. Phase Composition Studied by DTA and XRD

The calcined powders were checked by DTA and XRD. DTA is very sensitive to the most common impurity phases. As the impurity relations for the Y-Ba-Cu-O system have been established, phase purity may be identified by determining the melting point of the sample. Since the primary concern for low levels of impurity phases are those with low melting temperatures, this method is an ideal diagnostic technique.

DTA measurements were made from room temperature to 1000°C, at a scan rate of 3°C/min for calcined powders, using a Model TG 85-16-18 Setram, Differential Thermal Analyzer. The DTA scans were plotted by computer, and the results for Samples CZ-C and CZ-G are shown in Figure 13.

Phase analyses of calcined powders were done by XRD, using Cu K- α radiation in a General Electric X-Ray Diffractometer, Model 11GJ26A1, with a scan rate of 2°/min. The voltage and current used were 30 kV and 14 mA, respectively. The limit of the XRD resolution is about 2% by volume. The XRD pattern for the 123 powder is shown in Figure 14. As can be seen from this figure, only single phase 123 powders were found.

Figure 13. DTA Traces of Samples (a) Calcining in Air Twice at $900^{\circ}C$, (b) Calcining in Vacuum Twice at $850^{\circ}C$

Figure 14. XRD Patterns of Calcined Powders of 123

The results of the DTA and XRD measurements are summarized in Table 6.

Table 6. Impurity Phases in 123 Powders from Different Calcining Conditions

Sample No.	Liquid Phases (DTA Results)	Impurity Phases (XRD Results)
CZ - A	Phase-Pure	$p/p'' < 0.5$
CZ - B	Phase-Pure	$p/p' < 0.5$
CZ - C	Phase-Pure	$p/p' < 0.5$
CZ - D	Phase-Pure	$p/p' < 0.5$
CZ - E	Very slight liquid phases	$p/p' = 0.5$
CZ - F	Very slight liquid phases	$p/p' = 1$
CZ - G	Some liquid phases	$p/p' < 0.5$
CZ - H	Some liquid phases	$p/p' = 0.5$

* There are very minor BaCuO_2 phases, $p/p' = \text{BaCuO}_2 \text{ peak } (2\theta = 29.3^\circ) / 123 \text{ peak } (2\theta = 22.8^\circ)$

XRD and DTA results show that calcination in vacuum at 850°C and 900°C can yield very good powders. Previous experiments⁽⁶¹⁾ have also shown that phase-pure 123 powders can be synthesized by calcining in vacuum. Thus the lower temperature

(850°C), vacuum calcined powder was chosen as the second step experimental powder.

4.2. Sintering And Annealing

The powder, calcined at 850°C, in vacuum, was pressed into 1.2 grams, 12.7 mm diameter discs at a pressure of 138 MPA. The discs were placed on alumina setters and heated in a tube furnace to the given sintering temperature, held for 5 hours at the temperature, cooled to 450°C at a rate of 1°C/min, and held at this temperature for 12 hours and then cooled to room temperature. This annealing ensured the transformation from the tetragonal to the orthorhombic structure.

Four groups, each made up of four samples, were sintered at temperatures of 910, 940, 970 and 1000°C, respectively. Oxygen gas at ambient pressure was passed through the furnace during the entire process.

Sixteen groups, each made up of four samples, were sintered at temperatures of 910, 940, 970 and 1000°C, respectively, with CO₂/O₂ gas mixture, at ambient pressure, passed through the furnace during the entire process. The sintering conditions, i.e. temperature and CO₂/O₂ ratio were as listed in Table 4 (Section 3.1)

4.3. Testing

4.3.1. Density and J_c Measurement

After sintering, each sample was weighed and its external dimension were measured in order to calculate the density, which is reported in Section 5.1.1. The measured external dimensions and weights of the samples are listed in Appendix D. The theoretical density of 123 is 6.3 g/cm^3 .⁽⁶²⁾

Bars about 10 mm long and 1 mm^2 in cross-section were cut from each pellet. A standard four-point probe resistivity measurement was performed to test samples for critical current densities in zero magnetic field. A current of 0.1 A was passed through the sample at room temperature and the voltage drop across the sample was measured. The sample was then slowly immersed in liquid nitrogen (77 K), and the voltage drop again measured. For superconductors, the voltage drop at 77 K will be much lower than the drop at room temperature. If the voltage drop is larger at 77 K than at room temperature, the sample is a semiconductor. Usually a $1.0 \text{ } \mu\text{V/cm}$ voltage criterion was used to define the J_c values obtained.

4.3.2. T_c Measurement

Superconducting transition temperatures were measured for representative samples, using two methods: resistivity measurement and R. F. magnetization measurement. As was

mentioned in Section 1.1, superconducting materials have two basic and distinct characteristics: zero resistance and the Meissner effect which is the ability of a material to expel a magnetic field. The resistivity measurement illustrates the temperature dependence of the electrical resistance of the samples; the zero resistance is a visible benefit of superconductivity. Magnetization measurements are made by monitoring the temperature dependence of the diamagnetic signal produced by the sample: an abrupt change of susceptibility illustrates the Meissner effect.

The resistivity measurements were made by a standard four-point probe DC technique, in the temperature range of 77-300 K, by immersion in liquid nitrogen.

The R. F. magnetization was measured with a SQUID magnetometer. The samples were cooled in zero field, and then a magnetic field of 0.5 Oe was applied as the sample warmed. The temperature dependence of the magnetic susceptibility of the sample was qualitatively examined by measuring the change in inductance of a wire coil surrounding the sample. This technique allowed rapid identification of the sharpness and onset temperature of the superconducting transition.

4.3.3. Microstructure

Sintered samples were polished, using a diamond paste, down to 1 μm and examined by optical microscopy and scanning electron microscopy. The mean grain size of each sample was measured with optical micrographs, at 800 times magnification, using the line intercept method.

Representative samples for TEM were prepared by the following method. Three millimeter diameter discs were cut from bulk samples, and then thinned by dimpling plus ion-milling (5 kV, 1 mA per ion gun) on a liquid nitrogen cooled stage. These discs were then examined by a Philips CM 320 transmission electron microscope; the unit was equipped with an energy dispersive spectrometer. The microstructure and composition of the grains and grain boundaries were studied and recorded.

4.3.4. XRD Measurement

The phase composition of the sintered samples was studied by X-ray diffraction of powdered samples.

4.4. Reannealing

Samples sintered in 50 ppm, 500 ppm and 0.5% CO_2 containing atmospheres were reannealed in pure oxygen flow at 450°C for 15 hours, to check the reversibility of the second phases formed.

Samples sintered in pure oxygen flow were reannealed in oxygen flow with 5% CO₂ for 10 hours, to check the formation of second phases.

5. EXPERIMENTAL RESULTS

5.1. Effect Of Sintering Temperature And Atmosphere On Density And J_c

5.1.1. Sintering Temperature

The effects of sintering temperature on the density of the pellets and the critical current density for samples tested are shown in Figures 15 and 16 and Appendix E.

From Figures 15 and 16, it is noticed that the sintering temperature is a major factor affecting both the relative density and the critical current density, J_c . The relative density increased with the sintering temperature. Increased sintering temperatures also resulted in higher J_c values. The highest J_c , 320 A/cm², was recorded for samples with 92% theoretical density, sintered at 1000°C in 100% O₂.

5.1.2. Atmosphere

The sintering atmosphere was found to have practically no effect on the density of the 123 powders. However, when 5% CO₂ was added to the sintering atmosphere, the density of sample changed dramatically. The samples which were sintered above 970°C in 5% CO₂ + O₂ flow were found to be partially melted. For the 1000°C sintered samples, they were slightly deformed. The most obvious possibility is that the higher CO₂ content reduced the

Figure 15. The Effect of Sintering Temperature on Density

Figure 16. The Effect of Sintering Temperature on J_c

melting temperature of the sample, thereby causing the formation of liquid phases and increasing the density of the samples. Thus, it can be explained why the densities of the samples sintered at higher CO₂ contents, at 940 and 910°C, are higher than those of the samples sintered at the same temperature in lower CO₂ atmosphere. The grain size of the samples sintered in various CO₂ contents was found to be almost the same as that of the sample sintered in pure oxygen flow.

For the critical current density, the J_c values decrease as CO₂ content increases. These data are less than 200 A/cm² in all cases, with some samples having a J_c value of zero. In short, when the CO₂ content increases, the samples gradually alter their superconductive properties and eventually become non-superconductors.

The results of the reaction studies on YBa₂Cu₃O_{6+x} in CO₂ containing atmospheres are summarized in the log pCO₂ versus 1/T plot in Figure 17. The solid line in Figure 17 separates the stability regions of superconductors and semiconductors. The 123 superconductor is thus stable at higher temperatures and lower pCO₂.

Figure 17. Stability of 123 Compounds as a Function of p_{CO_2} and Temperature

The relationship between the partial pressure of carbon dioxide and temperature can experimentally be described as follows:

$$\log p_{CO_2} = C/T + D \quad (\text{Eq.16})$$

where $C = -45,000 \text{ K}$ and $D = 33.4$

The equilibrium diagram in Figure 17 outlines the restrictions on the procedures for the synthesis of 123 superconductors. The compound can be successfully sintered only under conditions to the left of the equilibrium boundary in Figure 17.

5.2. Microstructure

The microstructure of some typical samples are shown in Figures 18 and 19. The average grain size is below $2.5 \mu\text{m}$ in the material sintered below 940°C . Large grain growth, as shown in Figure 20, is observed at 970°C . This results in a large increase in density. From Figures 18 through 20, it can be seen that the denser samples have larger grain sizes, whereas the less dense, more porous, samples have smaller grain sizes. From this micrographic analysis, the J_c increase is thought to result from the increase in connectivity between grains.

Figure 18. Optical Micrographs for Samples Sintered under 100% O₂ at (a) 910°C, (b) 940°C, (c) 970°C and (d) 1000°C

Figure 19. SEM Micrographs of the Fracture for Samples Sintered under 100% O₂ at (a) 910°C, (b) 940°C, (c) 970°C and (d) 1000°C

Figure 20. Grain Size of Samples Sintered under 100% O₂

From Figure 21, it can also be seen that the crystals of the samples sintered in lower CO₂ atmospheres are twinned, whereas those sintered in 5% CO₂ do not show any twinning. As mentioned in Section 2.1, the twin structure in 123 determines its orthorhombic superconducting properties.⁽²⁶⁾ The samples sintered in 5% CO₂ are therefore not orthorhombic.

5.3. The Relationship Between T_c And Atmosphere

The superconducting properties investigated by both resistance and magnetization measurements are shown in Figures 22 and 23. With respect to both figures, sample (a) was sintered in pure O₂ flow, sample (b) sintered in 50 ppm CO₂ + O₂, and sample (c) sintered in 0.5% CO₂ + O₂. The superconducting phase transition of sample (a) drops sharply, with an onset at about 90 K and a zero resistance at 82 K. A linear temperature dependence of R, with $\partial R/\partial T > 0$, before the onset of superconductivity is observed, indicating that this sample is a good superconductor. The resistivity curve does not indicate the presence of a second superconducting transition. However, sample (b) shows two transitions one at 90 K and another one at 80 K. Zero resistivity is observed at about 78 K. The resistivity of sample (c) increases monotonically at temperatures below 300 K, that is $\partial R/\partial T < 0$. This sample shows quite marked semiconducting characteristics because of its R versus T curve. There is only one transition with onset of superconductivity at 85 K.

Figure 21. Optical Micrographs for Samples Sintered at 1000°C, with (a) Pure O_2 , (b) $O_2 + 50$ ppm CO_2 , (c) $O_2 + 0.5\%$ CO_2 and (d) $O_2 + 5\%$ CO_2

Figure 22. Resistivity vs Temperature for Samples Sintered at 940°C, with (a) Pure O₂, (b) O₂ + 50 ppm CO₂, (c) O₂ + 0.5% CO₂

Figure 23. R.F. Susceptibility vs Temperature for Samples Sintered at 940°C, with (a) Pure O_2 , (b) $O_2 + 50$ ppm CO_2 , (c) $O_2 + 0.5\%$ CO_2

It also can be seen that sample (b) is not quite as good as sample (a), with respect to its zero resistance transition temperature. In addition, the resistivity of sample (b) is always higher than that of sample (a). Comparing the resistivity data for these three samples, as shown in Figure 22, it is noted that as the CO₂ content increases the electrical resistivity of the sample, at 90~300 K, increases. This is in agreement with the findings of Wang et al.⁽⁶³⁾ who found that an increase in CO₂ content results in an increase of the Hall coefficient, and the findings of Hakazawa et al.⁽⁶⁴⁾ and Kwok et al.⁽⁶⁵⁾ who reported a decrease in oxygen content of the sample with increasing CO₂ contents.

Figure 23 shows the magnetization measurement made on sintered samples. The observed diamagnetism indicates that the major phase of these samples is still superconducting. Sample (a) contains a single superconducting phase with $T_c = 90$ K, whereas samples (b) and (c) contain two phases. Two diamagnetic signals appear in sample (b), one at 90 K, another at 80 K. This result is in agreement with the resistance measurement which indicated that there are two superconducting phases in sample (b). For sample (c), a weak diamagnetic signal appears at around 80 K. It is inferred that a 80 K phase probably exists in sample (c). On the other hand, the important feature to note in each of these plots is the non-linear tailing at the low temperature edge of the

superconducting transition, i.e. sample (a) with high J_c value exhibits a small, steep tail; samples (b) and (c) with low J_c values have broad, flat tails, which is due to chemical variations either in the bulk or at the grain boundaries.⁽¹⁾

However, the magnetization measurement of these three samples in Figure 23 cannot explain why J_c was found to be zero in some of the samples. Since CO_2 is present in the sintering atmosphere, it can be inferred that CO_2 leads to partial carbonation of the sample, and that these carbonated phases may accumulate along the grain boundaries. Although these samples consist of superconducting grains, these grains would then be isolated by some non-superconducting second phase which causes the J_c value to decrease strongly. This hypothesis was then checked by TEM.

5.4. Microstructure And Composition Determined By TEM

The composition at and near grain boundaries in typical sintered samples were investigated using TEM in conjunction with EDS. No evidence of second phases at grain boundaries was found in samples sintered in a 100% oxygen atmosphere. However, two distinct types of grain boundaries were observed in the samples that were sintered in 0.5% $\text{CO}_2 + \text{O}_2$. Approximately 10% of the grain boundaries were found to be wet by a thin layer of a second phase, as shown in Figure 24. As can be deduced from Figure 25, the EDS spectra obtained from locations along this boundary

Figure 24. Sample Sintered at 970°C in 0.5% CO₂ + O₂. TEM micrograph for the grain boundary, as marked by G.B., which is wet by a layer of BaCuO₂ second phase

Figure 25. EDS Spectrum Obtained from a Point in the Grain Boundary of a Sample Sintered in 0.5% CO₂ + O₂

indicated that the composition of this layer was rich in barium and copper, but poor in yttrium, and was likely to be eutectic BaCuO_2 . Also some layers were found to be very rich in copper; these layers may be $\text{BaCuO}_2 + \text{CuO}$ phases, according to the phase diagram. The remaining boundaries were sharp grain boundaries which were free from this second-phase. By using high-resolution transmission electron microscopy (HRTEM) imaging, it was also found that the structure near the sharp grain boundaries was not orthorhombic, but tetragonal. Figure 26 is a HRTEM image of a sharp grain boundary with a tetragonal phase. In this case, the lattice fringes in the $[001]$ direction are clearly observed in one grain. Measuring the spacing of lattice fringes, it was found that $c = 1.19$ nm near the grain boundary, whereas $c = 1.17$ nm in the region far from the grain boundary. From neutron diffraction data,⁽²⁰⁾ it is known that $c = 1.19$ nm for the tetragonal structure and $c = 1.17$ nm for the orthorhombic structure. The region having $c = 1.17$ nm was also found to have twin structures, whereas the region having $c = 1.19$ nm was found to have no twin structure. A boundary could be observed between these two regions. The orthorhombic phase exhibits twinning, but the tetragonal phase does not.⁽²⁶⁾ This was used as further evidence to come to the conclusion that the region adjacent to the grain boundaries is tetragonal, while the region further away is orthorhombic.

Figure 26. Sample Sintered at 970°C in 0.5% CO₂ + O₂. HRTEM image of a grain boundary (G.B.) whose normal is [001]. The lattice fringes of 1.19 nm spacing correspond to tetragonal structure (T); while the lattice fringes of 1.17 nm spacing correspond to orthorhombic structure (O). A twin structure, in O phase, terminates between tetragonal and orthorhombic phase boundary (P.B.)

Carbon concentration profiles, using secondary ion-mass spectroscopy (SIMS), were taken from samples sintered in 100% oxygen and 0.5% CO₂ + O₂ atmospheres. There was no clear indication of local carbon segregation at the grain boundaries or near grain boundaries for samples sintered in pure oxygen. However, a variation in carbon signal was observed near the grain boundary regions for the sample sintered in 0.5% CO₂ + O₂.

EDS also revealed the presence of precipitates of Y₂BaCuO₅ for the samples sintered in 0.5% CO₂, as shown in Figure 27. These second phase particles were observed to be rounded in shape. It is clear that the Y₂BaCuO₅ phase, along with BaCO₃ and CuO phases, exist in these samples due to the decomposition of 123 in the presence of CO₂.

From the TEM analysis, the grain boundaries of the sample sintered in 50 ppm CO₂ + O₂ were found to be free from second phases, and the tetragonal phase was not observed. Figure 28 shows one of the grain boundaries of the sample. However, since the J_c values of these samples are extremely low, it is not possible to state conclusively that none of the tetragonal phase exists in the samples. It seems reasonable to suggest that the tetragonal phase around the boundaries is very thin, perhaps a few monolayers, and therefore was difficult to detect.

Figure 27. TEM Micrograph for the Sample Sintered in 0.5% CO₂ + O₂. A second-phase, Y₂BaCuO₅ as marked by S, is precipitated in grains

Figure 28. HRTEM Image of A Grain Boundary in the Sample Sintered in 50 ppm $\text{CO}_2 + \text{O}_2$. The lattice fringes of 1.17 nm spacing correspond to [001] (**c** direction) and 0.38 nm spacing correspond to [010] (**b** direction) of the orthorhombic 123 phase.

For the samples sintered at 5% CO₂ + O₂, the initial 123 phase was found to be completely decomposed. EDS showed these products to be Y₂BaCuO₅, BaCO₃ and CuO. Figure 29 shows the TEM micrograph of the sample. This observation was confirmed by X-ray diffraction patterns, as shown in Figure 30.

5.5. Composition Determined By XRD

X-ray powder diffraction of the samples sintered in lower CO₂ (CO₂ ≤ 0.5%) atmosphere indicated that the major phase was orthorhombic YBa₂Cu₃O_{6+x} , with BaCuO₂ as a very minor phase. Since the limit of resolution for the X-ray diffraction is on the order of 2 volume %, it is reasonable to conclude that other second phases identified by TEM were not detected by X-ray diffraction.

However, as mentioned before, when 5% CO₂ was present, the 123 superconductor was completely decomposed. The results are shown in Table 7 and Figure 30.

The X-ray patterns in Figure 30 (a) show that 123 was completely decomposed, and within the limitations of the XRD, no trace of 123 was detected when sintered at 970, 940 and 910°C in 5% CO₂. Surprisingly, when a sample was heated at 1000°C in 5% CO₂, there was still some 123 phase left, as shown in Figure 30 (b).

Figure 29. TEM Micrograph for the Sample Sintered in 5% CO₂ + O₂. The 123 phase is completely decomposed to 211, BaCO₃ and CuO.

Figure 30. XRD Patterns of Decomposed Phases (a) Sample sintered at 940°C, no 123 left; (b) Sample sintered at 1000°C, initial phase 123 left. (Y = 211, B = BaCO_3 and C = CuO)

Table 7. X-Ray Diffraction for the Samples
Sintered in 5% CO₂ + O₂ Flow

Sintering Temperature (°C)	Phases Observed
1000	123, Y ₂ BaCuO ₅ , BaCO ₃ , CuO
970	Y ₂ BaCuO ₅ , BaCO ₃ , CuO
940	Y ₂ BaCuO ₅ , BaCO ₃ , CuO
910	Y ₂ BaCuO ₅ , BaCO ₃ , CuO

5.6. Reannealing

To check the reversibility of the second phase formation, all the samples sintered in various CO₂ atmospheres were reannealed in pure oxygen for 15 hours at 450°C. There was no change in densities and J_c values. This means temperatures on the order of 450°C are too low to remove the CO₂ from the boundaries.

Bulk, about 1 cm diameter and 3 mm thickness, and thin, 3 mm diameter and 125 μm thickness, samples sintered in 100% O₂ atmosphere were reannealed at 800°C in oxygen containing 5% O₂ for 10 hours. X-ray diffraction of the bulk samples exhibited peaks characteristic of 123 phases, whereas the thin samples had decomposed to Y₂Cu₂O₅, BaCO₃ and CuO. These results indicate that diffusion of CO₂ is most probably the rate limiting step in the

decomposition of the 123 phase. The effect of the diffusion process of CO_2 will be discussed in greater detail in Chapter 6.

6. DISCUSSION

6.1. Effect Of CO₂

The results show that J_c decreases with an increase in CO₂ content in the sintering atmosphere. The carbon signal was observed near the grain boundaries for the samples sintered in CO₂ containing atmospheres. These suggest that CO₂ plays a critical role in the phase relationships in the Y-Ba-Cu-O system.

6.1.1. Effect of Lower CO₂ Content (<0.5%)

Sintering in an atmosphere containing CO₂ apparently decreases the melting temperature of 123. As discussed in Section 2.3.2, YBa₂Cu₃O_{6+x} was decomposed when heated to 1028°C in oxygen at 1 atm pressure. However, in air which contains 300 ppm CO₂, the decomposition temperature of YBa₂Cu₃O_{6+x} is approximately 29°C lower, i.e. at 999°C.⁽⁴⁸⁾ Roth⁽⁶⁶⁾ also found that the lower melting behavior of 123 was caused by CO₂ containing atmosphere. Unfortunately, so far no YBa₂Cu₃O_{6+x}-CO₂ phase diagram has been established.

In the current investigation, CO₂ was also found to lower the decomposition temperature of 123. As discussed in Section 5.4, as the CO₂ content in the atmosphere increased, there was clear evidence of an increasing fraction of the BaCuO₂, CuO and Y₂BaCuO₅ second phases; these phases form during the decomposition of 123.

The phase diagram⁽⁵⁰⁾ shown in Figure 31 shows that 123 melts incongruently at 999°C in air and forms a liquid and Y_2BaCuO_5 (referred as "211"). The reverse reaction occurs as the temperature is decreased. The 211 phase and the liquid phase must coexist for the growth of the 123 phase. Once the 211 phase is trapped inside the 123 phase and separated from the liquid phase no more reaction occurs, and 211 will show up as a second phase with the 123 grains. During further cooling, there is a small variation in stoichiometry in the direction of $\text{BaCuO}_2 + \text{CuO}$, since

Figure 31. Section Through the Ternary Phase Diagram Along the Join $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ - Y_2BaCuO_5 (Ref. 50)

the 211 phase is trapped inside the 123 phase. Because of the occurrence of local variations in stoichiometry, the eutectic reaction takes place and BaCuO_2 and CuO form at the grain boundaries.

The 211 phase was observed in the grain of the sample which was sintered in 0.5% $\text{CO}_2 + \text{O}_2$ atmosphere at 970°C . Therefore, the melting temperature of 123 in an environment containing 0.5% CO_2 may be below 970°C . As expected, BaCuO_2 and CuO were found along the grain boundary of this sample. As shown in Figure 24, this grain boundary was so wide that it may have formed from a liquid phase during sintering.

The phase diagram shown in Figure 31 is for equilibrium conditions. If there is a small variation in stoichiometry across the sample, it is possible to observe various nonequilibrium mixtures of phases. In this work, it was found that the composition of 123 was slightly off stoichiometric when the sample was heated in atmosphere containing CO_2 . The reason for this is not very clear.

Variations in microstructure also appear to influence the superconducting properties of 123 compounds. Samples sintered at lower CO_2 content ($\text{CO}_2 \leq 0.5\%$) exhibited superconductivity according to RF SQUID magnetometer measurements, as shown in

Figure 23. However, the J_c value of these samples decreased significantly with increasing CO_2 content of the environments. Also the materials sintered in the higher CO_2 environments showed formation of the second phases. Therefore, it appears that the decomposition at the grain boundaries weakens the path for the current, thereby decreasing the overall J_c value. As an example, in Figure 24, the low melting eutectic liquid exhibits a low dihedral angle with the grains and wets the grain boundary. The wetting of the boundaries with this non-superconducting phase decreases the effective contact area between the superconducting grains and therefore greatly decreases J_c , as discussed above. The width of the second phase region, which is about 50 nm, is much larger than the coherence length of this material, which is 3.4 nm in the direction parallel to the basal plane, and 0.7 nm in the c -direction.⁽⁶⁷⁾ Therefore, these second phase layers block the passage of currents.

According to the experimental results, the crystallized Y_2BaCuO_5 phases were observed precipitated in the grain, and $\text{BaCuO}_2 + \text{CuO}$ were found coated on the grain boundaries. It can be inferred that the partial decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ at lower CO_2 ($\text{CO}_2 \leq 0.5\%$) content occurs with the formation of Y_2BaCuO_5 , BaCuO_2 and CuO according to the following reaction:

In Section 2.4, it was stated that the reactivity of BaO with other oxides is a major factor influencing the chemical reactivity of 123. Since carbon signals were observed near the grain boundary, it is possible that CO₂ near the grain boundaries reacted with BaCuO₂ to form BaCO₃ according to the following reaction;

The Gibbs free energy change of Equation 18 is:

$$\begin{aligned} \Delta G_{298} &= \Delta G^\circ_{298} + RT \ln \frac{1}{p_{CO_2}} \\ &= -34,913 \text{ cal/mol} \end{aligned} \quad (\text{Eq.19})$$

where $\Delta G^\circ_{298} = -38,050 \text{ cal/mol}$,⁽⁵⁷⁾ and $p_{CO_2} = 0.5\% = 0.005 \text{ atm}$. Although EDS cannot distinguish between BaCO₃ and CuO signals from a BaCuO₂ signal, from ΔG_{298} values (which are negative), it is reasonable to conclude that Reaction 18 occurs. This result has been confirmed by previous investigators. Schrott et al.⁽⁶⁸⁾ reported from their x-ray photoemission spectroscopy study that the carbon was in the form of BaCO₃.

The reaction of CO_2 on the grain boundaries and formation of BaCO_3 can also explain the presence of the tetragonal structure observed near the grain boundaries in Figure 26. When heated in a CO_2 environment, the 123 grain boundaries were coated by some BaCO_3 second phase. As was mentioned in Section 2.1, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is tetragonal at high temperature and undergoes an order-disorder transition at about 650°C to the low-temperature orthorhombic phase. This transition occurs because of oxygen diffusion. However, the presence of the crystallized BaCO_3 on the grain surface would serve as an oxygen diffusion barrier. As the tetragonal phase can be obtained at room temperature by quenching from above the phase transition temperature, the high temperature tetragonal phase was probably preserved at the grain boundaries by the presence of BaCO_3 coated on the grain boundaries. Thus, BaCO_3 second phase coating was probably responsible for the fact that the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ near the grain boundaries was tetragonal after melting.

The suggestion of oxygen depletion of the tetragonal phase can also account for the plots of Figure 23, which show that in samples sintered at lower CO_2 ($<0.5\%$) content, the major phase is superconducting. However, the slight stoichiometric variations decrease the superconducting transition temperature. In Figure 23, sample (a) which was sintered in pure oxygen flow has a T_c of 90 K. According to Figure 4, the oxygen content in sample (a) is about 6.9

to 7.0 atoms per unit cell. Sample (b) which was sintered in 50 ppm $\text{CO}_2 + \text{O}_2$ flow has a T_c at 80-90 K. The oxygen content in sample (b) is 6.8 atoms per unit cell. Sample (c) which was sintered in 0.5 % $\text{CO}_2 + \text{O}_2$ flow has a T_c about 80 K. The oxygen content in sample (c) is 6.7 atoms per unit cell. It has been noted that a decrease of oxygen content of the sample, with increasing CO_2 content in the sintering atmosphere, is related to the decreasing trend of the T_c value. Also as the oxygen content of the sample decreases with increasing CO_2 content in the sintering atmosphere, the sample gradually changes its structure from orthorhombic to tetragonal.

The slightly altered composition of the sample can also be observed from the tails of the plots below 90 K in Figure 23. The superconducting transition is very sharp for the sample which is pure and structurally perfect. But if the sample is impure, the transition is broad.⁽¹⁾ Thus the high oxygen content and the high purity of the sample is responsible for the short, steep tail of the plot, whereas the low oxygen content and impurity of the sample is responsible for the long, flat tail. As an example, sample (b) which was sintered at 50 ppm $\text{CO}_2 + \text{O}_2$ presented two superconducting phases with different T_c 's. The phase with the higher T_c has a higher oxygen content, whereas the phase with the lower T_c has a lower oxygen content. It is the lower oxygen content phase that responds with a long flat tail of the transition properties. This

assumption is supported by the report of Greenlief et al.⁽⁶⁹⁾, who suggested that the presence of impurities or non-superconducting phases influences the superconducting transition form. As impurities or non-superconducting phases were decreased, the superconducting transition sharpens.

In summary, sintering under atmospheres containing CO₂ will lead to partial decomposition near the grain boundaries of the sample. These non-superconducting boundaries act as an S-N-S junction, and thereby impede the current path. At the same time, the partial decomposition results in oxygen depletion of the sample. The lower oxygen content is responsible for the tetragonal structure which also reduces the superconducting properties.

6.1.2. Reaction with Higher CO₂ Content (≈5%)

Since the superconducting 123 phase is highly sensitive to CO₂, when the CO₂ content increases to a certain value, this phase will be carbonated. The reaction is given by Equation 20.

From this investigation, it was found that the sintering temperature is also an important factor. As shown in Table 7, at p_{CO₂}<1, 123 is more susceptible to carbonation at lower

temperatures than at higher temperatures. This phenomenon can be explained by the thermodynamics of the reaction. By assuming that the activity of the pure solid phases is equal to unity, the Gibbs free energy, ΔG , change of Equation 20 can be expressed as:

$$\Delta G = \Delta G^\circ + RT \ln \frac{(p_{O_2})^\delta}{(p_{CO_2})^3} \quad (\text{Eq.21})$$

Since p_{O_2} tends to 1 atm ($p_{O_2} = 0.95$) and $0 < \delta < 0.5$, Equation 21 can be simplified as following:

$$\begin{aligned} \Delta G &= \Delta G^\circ - RT \ln (p_{CO_2})^3 \\ &= \Delta G^\circ - 3RT \ln p_{CO_2} \end{aligned} \quad (\text{Eq.22})$$

At equilibrium $\Delta G = 0$, and therefore:

$$\Delta G^\circ = 3RT \ln p_{CO_2} \quad (\text{Eq.23})$$

Since as T increases, p_{CO_2} must increase to maintain the same ΔG° value. This holds for values of $p_{CO_2} < 1$. Therefore, increasing the temperature can raise the CO_2 partial pressure.

6.2. Effect Of Sintering Temperature

As discussed above, increasing sintering temperatures can raise the equilibrium CO_2 partial pressure. On the other hand, high sintering temperatures lead to high density of the ceramic

superconductor, improving contact between the grains. Increased J_c with increasing sintering temperature, therefore, can be expected.

It was stated in Section 2.3.2 that it is very difficult to obtain densities very close to theoretical density by solid-state sintering. For sintering temperatures below 940°C, sintering is dominated by solid-state diffusion and the resulting specimens were very porous. This decreases the cross sectional area for carrying the current, thus limiting the overall J_c . Increasing the sintering temperature causes a change from solid-state diffusion to liquid-phase sintering. Slight liquid-phase sintering is beneficial for the J_c value, since slight liquid-phase sintering increases the sample density. However, the J_c value at the higher temperatures seems to be determined by the presence of the liquid phase. If the composition of the liquid does not solidify to a superconducting phase, then this produces insulating grain boundaries, thus limiting the transport current.

6.3. Reaction At Different Temperatures

According to this investigation, the reaction of 123 with CO_2 at temperatures above 910°C at 5% CO_2 is given by Equation 20. Reaction processing of 123 with CO_2 is complicated in this four phase system. The $\text{Y}_2\text{O}_3\text{-BaO-CuO}$ composition diagram, Figure 6(a), illustrates coexisting phases. It is noted that 123 only coexists

with 211, BaCuO₂ and CuO at 950-1000°C. There are no tie-lines from 123 through Y₂Cu₂O₅, so that at this temperature Y₂Cu₂O₅ is unstable. On the other hand, since there exists CO₂ in the sintering/annealing atmosphere, BaCuO₂ reacts with CO₂ to form BaCO₃ and CuO. Therefore, the complete reaction of 123 with CO₂ above 910°C is given by Equation 20.

The results of experiment show that 123 was decomposed to BaCO₃, Y₂Cu₂O₅ and CuO when annealed at 800°C in 5% CO₂ + O₂ flow. Thus at 800°C the reaction is as follows:

According to the result, the Y₂Cu₂O₅ phase appears to be stable at a sintering temperature of 800°C, in 5% CO₂ atmosphere. Also according to the standard Gibbs free energy of formation of Y₂Cu₂O₅, $\Delta G^\circ_{1073} = -4,960 \text{ J mol}^{-1}$, as reported by Kale and Jacob,⁽⁷⁰⁾ Y₂Cu₂O₅ is stable at 800°C. Therefore, it is possible that Y₂Cu₂O₅ coexists with BaCuO₂ and CuO at that temperature. This result is in agreement with the results of Fjellvåg et al.,⁽⁴⁷⁾ who reported that above 730°C, the reaction products of 123 with CO₂ are BaCO₃, Y₂Cu₂O₅ and CuO.

6.4. Diffusion Of CO₂

As discussed in Section 5.6, the thermally activated processes that occur in 123 decomposition are diffusion controlled processes, and the rate of the processes is determined by the diffusion of CO₂; strictly speaking, it is determined by the diffusion of carbon ions. Two processes are necessary for CO₂ reaction with 123: (1) diffusion of CO₂ to the grain boundaries and reaction with 123 to form the carbonate, (2) diffusion of carbon ions through the BaCO₃ and 123 interface to 123 grains.

The structure of BaCO₃ is orthorhombic⁽⁷¹⁾ in which the carbon atom occupies the (1/2, 1/2, 1/2) site. The diffusion mechanism for carbon ions from BaCO₃ to 123 is interstitial diffusion, since the radius of C⁴⁺, which is 0.16Å, is smaller compared to that of O²⁻ and Ba²⁺, which are 1.32Å and 1.34Å respectively.⁽¹³⁾ The general expression for diffusion process is given by Fick's First Law:

$$J = -D \frac{\Delta C}{\Delta x} \quad (\text{Eq.25})$$

where $\Delta C/\Delta x$ is the concentration gradient, D is the carbon diffusion coefficient. J is the net flux of diffusing solute atoms. The minus sign is necessary, since the diffusion occurs down a concentration gradient.

This expression merely states that in the presence of a uniform concentration gradient the flux of diffusion atoms is proportional to the product of the diffusion coefficient and the concentration gradient. Since the diffusion coefficient, D , is a function of temperature, i.e. $D = D_0 \exp(-\Delta G/RT)$, as the temperature is raised, the diffusion rate increases. The concentration gradient, $\frac{\Delta C}{\Delta x}$, is the driving force for atomic diffusion. Thus increasing $\frac{\Delta C}{\Delta x}$ can also increase diffusion rate.

According to the Equation 25, the results given by the Section 5.6 are reasonable. To achieve a large diffusion rate, high temperature is required. If no sufficient temperature is allowed for carbon atoms to move fast, the diffusion rate is very slow. This is the reason that within 15 hours and 450°C annealing no change in the densities and J_c values was observed.

For the bulk and thin samples which were reannealed at 800°C in 5% $\text{CO}_2 + \text{O}_2$ flow, although the diffusion coefficients D have the same value, the concentration gradient $\Delta C/\Delta x$ of the thin sample is much larger than that of bulk sample. This is because Δx which is the thickness of the sample is much smaller of the thin sample than of the bulk sample. Thus at the same period, the thin sample was decomposed, whereas the bulk sample was not.

7. CONCLUSIONS

The present study has shown that the 123 compound can only be successfully prepared from BaCO_3 and oxides under the conditions to the left of the equilibrium boundary in Figure 17. The critical current density of 123 strongly depends on the sintering conditions. The results of this work indicate the following:

- (1) Sintering atmospheres containing CO_2 strongly reduce J_c , $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ reacts with CO_2 and results in lower melting phases and compositional inhomogeneity which accumulates at grain boundaries, thereby impeding the current path. Thus, sintering in air which contains 300 ppm CO_2 and/or commercially pressurized oxygen, which contains approximately 30 ppm CO_2 , will restrict J_c .
- (2) The tendency of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ superconductor material towards carbonation also depends on the temperature of reaction. Increasing temperatures raise the equilibrium CO_2 partial pressure, so that 123 is less susceptible to carbonation at higher sintering temperatures, such as 1000°C , than at lower sintering temperatures.
- (3) In atmospheres containing higher levels of CO_2

($\text{CO}_2 > 5\%$), the reaction products also depend on reaction temperature. At temperatures above 910°C , 123 is decomposed to Y_2BaCuO_5 , BaCO_3 and CuO ; at 800°C , 123 is decomposed to $\text{Y}_2\text{Cu}_2\text{O}_5$, BaCO_3 and CuO .

REFERENCES

1. Omar, M. A., Elementary Solid State Physics, Lowell Technological Institute, (1985), p 496.
2. London, F., Superfluids. Macroscopic Theory of Superconductivity, V. 1, John Wile & Sons, New York, (1950), p 27.
3. Bardeen, J., Cooper, L. N. and Schreiffer, J. R., "Theory of Superconductivity," Phys. Rev., 108, (1957), p 1175.
4. Kunzler, J. E., Buehler, E., Hsu, F. S. L. and Wernick, J. H., "Superconductivity at High Current Density in a Magnetic Field of 88 Kgauss," Phys. Rev. Lett., 6, (1961), p 89.
5. Bednorz, J. G. and Muller, K. A., "Possible High T_c Superconductivity in the Ba-La-Cu-O System," Z. Phys., B 64, (1986), p 189.
6. Uchida, S., Tagagi, H., Kitazawa, K. and Tanaka, S., "High T_c Superconductivity of La-Ba-Cu Oxides," Jap. J. Appl. Phys., 26, (1987), p L1.
7. Zhao, Z. X., Chen, L. Q., Cui, C. G., Huang, Y. Z., Liu, J. X., Chen, G. H., Li, S. L., Guo, S. Q. and He, Y. Y., "High T_c Superconductivity of Sr(Ba)-La-Cu Oxides" Kexue Tongbao, 32, (1987), p 522.
8. Chu, C. W., Hor, P. H., Meng, R. L., Gao, L., Huang, Z. J. and Wang, Y. Q., "Evidence for Superconductivity above 40 K in the La-Ba-Cu-O Compound System," Phys. Rev. Lett., 58, (1987), p 405
9. Wu, M. K., Ashburn, J. R., Torng, C. J., Hor, P. H., Meng, R. L., Tao, L., Huang, Z. J., Wang, Y. Q. and Chu, C. W., "Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Commppound System at Ambient Pressure," Phys. Rev. Lett., 58, (1987), p 908.
10. Maeda, H., Tanaka, Y., Fukutomi, M. and Asano, T., "A New High- T_c Oxide Superconductor without a Rare Earth Element," Jap. J. Appl. Phys., 27, (1988), p L209.

11. Gao, L., Huang, J., Meng, R. L., Hor, P. H., Bechtold, J. Sun, Y. Y., Chu, C. W., Sheng, Z. Z. and Hermann, A. M., "Bulk Superconductivity In $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_{8+\delta}$ up to 120 K," Nature, 332, (1988), p 623.
12. Sheng, Z. Z., Hermann, A. M., El Ali, A., Almasan, C., Estrada, J., Datta, T. and Matson, R. J., "Superconductivity at 90 K in the Ti-Ba-Cu-O System," Phys. Rev. Lett., 60, (1988), p 937.
13. Charles, P. P., Timir, D. and Horacio, A. F., Copper Oxide Superconductors, Jon Wiley & Sons, New York, (1988), p 7.
14. Clarke, J., "Small-Scale Analog Applications of High-Transition-Temperature Superconductors," Nature, 333, (1988), p 29.
15. Firth, I. M., Superconductivity, Mills & Boon Limited, London, (1972), p 8.
16. McGuire, T. R., Dinger, T. R., Freitas, P. J. P., Gallagher, W. J., Plaskett, T. S., Standstrom, R. L. and Shaw, T. M., "Magnetic Properties of Y-Ba-Cu-O Superconductors," Phys. Rev., B 36, (1987), p 4032.
17. Sun, J. Z., Webb, D. J., Naito, M., Char, K., Hahn, M. R., Hsu, J. W. P., Kent, A. D., Mitzi, D. B., Oh, B., Beasley, M. R., Geballe, T. H., Hammond, R. H. and Kapitulnik, A., "Superconductivity and Magnetism in the High- T_c Superconductor Y-Ba-Cu-O," Phys. Rev. Lett., 58, (1987), p 1574.
18. Cava, R. J., Batalogg, B., Van Dover, R. B., Murphy, D. W., Sunshine, S., Siegrist, T., Remeika, J. P., Rieteman, E. A., Zahurak, S. M. and Espinosa, G. P., "Bulk Superconductivity at 91 K in Single-Phase Oxygen-Deficient Perovskite $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$," Phys. Rev. Lett., 58, (1987), p 1676.
19. Beno, M. A., Soderholm, L., Capone II, D. W., Hinks, D. G., Jorgensen, J. D., Grace, J. D., Schuller, I. K., Segre, C. U. and Zhang, K., "Structure of Single-Phase High-Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Appl. Phys. Lett., 51, (1987), p 57.

20. Cava, R. J., Batlogg, B., Chen, C. H., Rietman, E. A., Zahurak, S. M. and Werder, D., "Single-phase 60-K Superconductor in Annealed $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ ($0.3 < \delta < 0.4$) with Correlated Oxygen Vacancies in the Cu-O Chains," Phys. Rev., B 36, (1987), p 5719.
21. Jorgensen, J. D., Beno, M. A., Hinks, D. G., Soderholm, L., Volin, K. J., Hitterman, R. L., Grace, J. D., Schuller, Ivan. K., Segre, C. U., Zhang, K. and Kleefish, M. S., "Oxygen Ordering and the Orthorhombic-to-Tetragonal Phase Transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," Phys. Rev., B 36, (1987), p 3608.
22. Jorgensen, J. D., Veal, B. W., Kwok, W. K., Crabtree, G. W., Umezawa, A., Nowicki, L. J. and Paulikas, A. P., "Structural and Superconducting Properties of Orthorhombic and Tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: The Effect of Oxygen Stoichiometry and Ordering on Superconductivity," Phys. Rev., B 36, (1987), p 5731.
23. Kwok, W. K., Crabtree, G. W., Umezawa, A., Veal, B. W., Jorgensen, J. D., Malik, S. K., Nowicki, L. J., Paulikas, A. P. and Nunez, L., "Electronic Behavior of Oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Phys. Rev., B 37, (1988), p 106.
24. Shi, D. and Capone II, D. W., "60-90 K Superconducting Phase Transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Appl. Phys. Lett., 53, (1988), p 159.
25. Van Tendeloo, G., Zandbergen, H. W. and Amelinckx, S., "Electron Diffraction and Electron Microscopic Study of Ba-Y-Cu-O Superconducting Materials," Solid State Commun., 63, (1987), p 389.
26. Syono, Y., Kikuchi, M., Oh-ishi, K., Hiraga, K., Arai, H., Matsui, Y., Kobayashi, N., Sasaoka, T. and Muto, Y., "X-Ray and Electron Microscopic Study of a High Temperature Superconductor $\text{Y}_{0.4}\text{Ba}_{0.6}\text{CuO}_{2.2}$ " Jap. J. Appl. Phys. 26, (1987), p L498.
27. Hoff, H. A. and Pande, C. S., "Twins in High T_c Superconductors," Studies of High Temperature Superconductors, V. 3, Ed. by A. Narlikar, (1989), p 333.

28. Gray, K. E., Kampwirth, R. T., Murduck, J. M. and Capone II, D. W., "Experimental Study of the Ultimate Limit of Flux Pinning and Critical Currents in Superconductors," Physica, C 152, (1988), p 445.
29. Doss, J. D., Engineering's Guide to High-Temperature Superconductivity, John Wiley & Sons, New York, (1989), p 72.
30. Jin, S., Tiefel, T. H., Sherwood, R. C., Davis, M. E., Van Dover, R. B. Kammlert, G. W. and Keith, H. D., "High Critical Currents in Y-Ba-Cu-O Superconductors," Appl. Phys. Lett., 52, (1988), p 2074.
31. Kwak, J. F., Venturini, E. L., Nigrey, P. J. and Ginley, D. S., "Evidence for Homogeneous Superconducting Grains in High- T_c Oxides," Phys. Rev., B 37, (1988), p 9749.
32. Babcock, S. E., Kelly, T. F., Lee, P. J., Lavanier, L. A. and Larbalestier, D. C., "Investigation of Composition Variations near Grain Boundaries in High-Quality Sintered Samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Physica, C 152, (1988), p 25.
33. Nakahara, S., Fisanick, G. J., Yan, M. F., Van Dover, R. B. and Boone, T., "On the Defect Structure of Grain Boundaries in $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$," J. Crystal Growth, 85, (1987), p 639.
34. Camps, R. A., Evetts, J. E., Glowacki, B. A., Newcomb, S. B. and Stobbs, W. M., "The Role of Grain Boundaries in the Superconducting Properties of Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," J. Mater. Res., 2, (1987), p 750.
35. Kogure, T., Zhang, Y., Levonma, A., Kontra, R., Wang, W. X., Rudman, D. A., Yurek, G. J. and Vander Sande, J. B., "Grain Boundary Structure of $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ Formed by Oxidation of Metallic Precursors," Physica, C 156, (1988), p 707.
36. Dimos, D., Chaudhari, P., Mannhart, J. and LeGoues, F. K., "Orientation Dependence of Grain-Boundary Critical currents in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Bicrystals," Phys. Rev. Lett., 61, (1988), p 219.

37. Blendell, J. E., Handwerker, C. A., Vaudin, M. D. and Fuller Jr, E. R., "Composition Control of the Microstructure of $\text{Ba}_2\text{YCu}_3\text{O}_{6+x}$," J. Crystal Growth, 89, (1988), p 93.
38. Farrell, D. E., Chandrasekhar, B. S., DeGuire, M. R., Fang, M. M., Kogan, V. G., Clem, J. R. and Finnemore, D. K., "Superconducting Properties of Aligned Crystalline Grains of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Phys. Rev., B 36, (1987), p 4025.
39. Jin, S., Tietel, T. H., Sherwood, R. C., Van Dover, R. B., Daris, M. E., Kammlott, G. W. and Fastnacht, R. A., "Melt-Textured Growth of Polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with High Transport J_c at 77 K," Phys. Rev., B 37, (1988), p 7850.
40. Trolier, S. E., Atkinson, S. D., Fuierer, P. A., Adair, J. H. and Newnham, R. E., "Dissolution of $\text{YBa}_2\text{Cu}_3\text{O}_{(7-x)}$ in Various Solvents," Am. Ceram. Soc. Bull., 67, (1988), p 759.
41. Shibata, S., Kitagawa, T., Okazaki, H., Kimura, T. and Murakami, T., "Superconducting Oxides by the Sol-Gel Method Using Alkoxides," Jap. J. Appl. Phys., 27, (1988), p L53.
42. Barboux, P., Tarascon, J. M., Green, L. H., Hull, G. W. and Bagley, B. G., "Bulk add Thick Films of the Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Made by Controlled Precipitation and Sol-Gel Processes," J. Appl. Phys., 63, (1988), p 2725.
43. Bunker, B. C., Voigt, J. A., et al., "Precipitation of Superconductor Precursor Powders," High-Temperature Superconducting Materials, Marcel Dekker, Inc., New York and Basel, (1988), p 121.
44. William, J. et al., "Oxalate Precipitation Methods for Preparing the Yttrium-Barium-Copper Superconducting Compound," High-Temperature Superconducting Materials, Marcel Dekker, Inc., New York and Basel, (1988), p 153.
45. Poeppel, R. B., Balachandran, U., Bloom, I., Dorris, S. E., Dusek, J. T., Goretta, K. C., Lanagan, M. T., Leu, H. J., Maroni, V. A., Picciolo, J. J., Shi, D., Singh, J. P. and Youngdahl, C. A., "Recent Improvements in Bulk Properties of Ceramic Super-

- conductors," TMS Annual Meeting, Las Vegas, NV, Feb. 27-Mar. 3, (1989).
46. Nan Chen, "Study on the Sintering of $\text{YBa}_2\text{Cu}_3\text{O}_x$," M. S. Thesis, Illinois Institute of Technology, Illinois, (1988).
 47. Fjellvåg, H., Karen, P., Kjekshus, A., Kofstad, P. and Norby, T., "Carbonatization of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$," Acta Chemica Scandinavica, A 42, (1988), p 178.
 48. McCallum, R. W., "Critical Parameters in Processing $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$," Journal of Metal, January (1989), p 50.
 49. Gallagher, P. K., Grader, G. S. and O'Bryan, H. M., "Some Effects of CO_2 , CO and H_2O upon the Properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$," Mat. Res. Bull., 23, (1988), p 1491.
 50. Laudise, R. A., Schneemeyer, L. F. and Barns, R. L., "Crystal Growth of High Temperature Superconductors-Problems, Successes, Opportunities," J. Crystal Growth, 85, (1987), p 569.
 51. Chen, N., Shi, D. and Goretta, K. C., "Influence of Oxygen Concentration on Processing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," J. Appl. Phys., 66, (1989), p 2485.
 52. Tu, K. N., Tsuei, C. C., Park, S. I. and Levi, A., "Oxygen Diffusion in Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Oxides in Ambient Helium and Oxygen," Phys. Rev., B 38, (1988), p 772.
 53. Gopalakrishnan, I. K., Yakhmi, J. V. and Iyer, R. M., "Zero Electrical Resistance at 106 K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," Nature, 327, (1987), p 604.
 54. Shi, D., Capone II, D. W., Goretta, K. C., Zhang, K. and Gousdey, G. T., "A Time-Temperature-Transformation Diagram for the Orthorhombic to Tetragonal Phase Transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," J. Appl. Phys., 63, (1988), p 5411.

55. Barkatt, A., Hojaji, H. and Michael, K. A., "Reactions of Barium-Yttrium-Copper Oxides and Aqueous Media and Their Applications in Structural Characterization," Adv. Ceram. Mater., 2, (1987), p 701.
56. Frase, K. G., Liniger, E. G. and Clarke, D. R., "Environmental and Solvent Effects on Yttrium Barium Cuprate ($Y_1Ba_2Cu_3O_x$)," Adv. Ceram. Mater., 2, (1987), p 698.
57. Weast, R. C., CRC Handbook of Chemistry and Physics, 68th, CRC Press, Inc. Boca Raton, Florida, (1988), p D-53.
58. Bansal, N. P. and Sandkuhl, A. L., "Chemical Durability of High-Temperature Superconductor $YBa_2Cu_3O_{7-x}$ in Aqueous Environments," Appl. Phys. Lett. 52, (1988), p 323.
59. Goretta, K. C., Ira Bloom, Nan Chen, Goudey, G. T., Hash, M. C., Klassen, G., Lanagan, M. T., Poeppel, R. B., Singh, J. P., Shi, D., Balachandran, U., Dusek J. T. and Capone II, D. W., "Calzination of $YBa_2Cu_3O_{7-x}$ Powder," Materials Letters, 7, (1988), p 161.
60. Poppel, R. B., Flandermeyer, B. K., Dusek, J. T. and Bloom, I. D., "Fabrication of $YBa_2Cu_3O_7$ Superconducting Ceramics," Chemistry of High-Temperature Superconductors, American Chemistry Society, Symmposium Series 351, (1987), p 261.
61. Balachandran, U, Poeppel, R. B., Emerson, J. E., Johnson, S. A., Lanagan, M. T., Yonngdahl, C. A., Shi, D., Goretta, K. C. and Eror, N. G., "Synthesis of Phase-Pure Orthorhombic $YBa_2Cu_3O_x$ under Low Oxygen Pressure," Materials Letters, 8, (1989), p 454.
62. Wong-Ng, W., Roth, R. S., Swartzendrober, L. J., Bennel, L. H., Chiang, C. K., Beech, F. and Hubbard, C. R., "X-ray Powder Characterization of $Ba_2YCu_3O_{7-x}$," Adv. Ceram. Mater., 2, (1987), P 565
63. Wang, Z. Z., Clayhild, J., Ong, N. P., Tarascon, J. M., Green, L. H., McKinnon, W. R. and Hull, G. W., "Variation of $YBa_2Cu_3O_{7-y}$ Superconductivity with Carrier Concentration in Oxygen-Doped," Phys. Rev., B 36, (1987), p 7222.

64. Nakazawa, Y and Ishikawa, M., "Effects of Oxygen Stoichiometry and Oxygen Ordering in $\text{Ba}_2\text{YCu}_3\text{O}_y$ ($6 \leq y \leq 7$)," Physica, C 158, (1989), P 381.
65. Kwok, R. S., Cheong, S.-W., Thompson, J. D., Fisk, Z., Smith, J. L. and Willis, J. O., "Perspective on $\text{YBa}_2\text{Cu}_3\text{O}_x$ Materials from Oxygen Deficiency Studies," Physica, C 152, (1988), p 240.
66. Roth, R. S., Rawn, C. J., Beech, F., Whittler, J. D. and Andersson, J. O., "Phase Equilibria in the System Ba-Y-Cu-O- CO_2 in Air," Cerami Superconductors II, Ed. by Man F. Yan, (1988), p 13.
67. Worthington, T. K., Gallagher, W. J. and Dinger, T. R., "Anisotropic Nature of High-Temperature Superconductivity in Single-Crystal $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$," Phys. Rev. Lett., 59, (1987), p1160.
68. Schrott, A. G., Cohen, S. L., Dinger, T. R., Himpsel, F. J., Yarmoff, J. A., Frase, K. G., Park, S. I. and Purtell, R., "Photoemission Study of Grain-Boundary Segregation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," Thin Film Processing and Characterization of High-Temperature Superconductors, (1988), p 349.
69. Greenlief, C. M., Bringley, J. F., Gates, S. M., Scott, B. A., Trail, S. S. and D'Emic, C., "In-Situ Processing and Reaction of CO_2 with $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," Final Program and Abstracts, 1989 Fall Meeting of MRS, p 437.
70. Kale, G. M. and Jacob, K. T., "Gibbs Energy of Formation of CuYO_2 and $\text{Cu}_2\text{Y}_2\text{O}_5$ and Phase Relations in the System Cu-Y-O," Chem. of Mater., (1989), p 515.
71. Donnay, J. D. H. and Nowacki, W., Crystal Data, Published by the Geological Society of America, 1954.
72. Doss, J. D., Engineer's Guide to High-Temperature Superconductivity, John Wiley & Sons, New York, (1989), p 66,79.

BIBLIOGRAPHY

Bever, Michael B., Encyclopedia of Materials Science And Engineering, V. 1 & 4., Michael B. Bever, Massachusetts Institute of Technology, (1986).

Firth, I. M. Superconductivity, Mills & Boon Limited, London, (1972).

Phillips, J. C., Physics of High- T_c Superconductors, AT & T Bell Laboratories Murray Hill, New Jersey (1989).

Simon, R. and Smith, A. Superconductor. Conquering Technology's New Frontier, Plenum Press, New York, (1988).

APPENDIX A

Summary of the Characteristics of Type I and Type II Superconductors⁽⁷²⁾

Type I	Type II
Thermodynamic Field: H_c	Critical Fields: H_{c1} , H_{c2} , H_{c3}
Exhibits Intermediate State	Quantized Vortex Lines, Mixed State
Generally Pure Elements (e.g. Hg, Pb)	Generally Compounds (e.g. Nb_3Sn , $YBa_2Cu_3O_7$)
Lower Critical Currents	Higher Critical Currents*
Lower Critical Fields	Higher Critical Fields
Coherence Length (ξ) $\gg$ Penetration depth (λ)	Coherence Length (ξ) $\ll$ Penetration depth (λ)
Surface Current Flow for $H < H_c$	Bulk Current Flow for ($H_{c2} > H > H_{c1}$)
Transition temperature $T_c < 9.5$ K	Transition temperature $T_c < 130$ K

* The high- T_c copper oxide superconductors are Type II materials, but unlike most Type II superconductors, these ceramics have relatively low values of J_c in bulk samples. This is apparently due to grain-boundary effects, the presence of impurities, and other effects that depend largely upon processing.

APPENDIX B

Calculation of Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Partial Pressure of CO_2

According to Eq. 6:

$$\begin{aligned}\log p_{\text{CO}_2} &= -\frac{8900}{T} + 5.7 \\ &= -8900/1173 + 5.7 \\ &= -1.89\end{aligned}$$

For $T = 900 + 273 = 1173 \text{ K}$, then $p_{\text{CO}_2} = 0.02 = 2\%$

APPENDIX C

Calculation of Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Respect to Partial Pressure of O_2

According to Eq. 8:

$$\log p_{\text{O}_2} = - 8350/T + 8.0$$

(i) In pure oxygen (1.00 atm.)

$$\log 1 = - 8350/T + 8.0$$

$$T = 1043.75 \text{ K} \quad \text{or} \quad T = 770.75^\circ\text{C}$$

(ii) In air (79% N_2 , 21% O_2)

$$\log \frac{21}{100} = - 8350/T + 8.0$$

$$T = 962.23 \text{ K} \quad \text{or} \quad T = 689.23^\circ\text{C}$$

APPENDIX D

The Average Weight and Volume of the Samples

Sintering Conditions		External Dimension of the Sample		Sample Weight (g)	Sample Density (g/cm ³)
Sintering Temperature (C°)	CO ₂ Content	Diameter (cm)	Highness (cm)		
1000	0 *	1.056	.228	1.17	5.86
970	0	1.100	.231	1.20	5.48
940	0	1.216	.259	1.27	4.22
910	0	1.256	.246	1.21	3.97
1000	50 ppm	1.060	.233	1.19	5.80
970	50 ppm	1.114	.235	1.24	5.42
940	50 ppm	1.217	.253	1.24	4.21
910	50 ppm	1.260	.245	1.19	3.89
1000	500 ppm	1.064	.244	1.26	5.82
970	500 ppm	1.113	.232	1.23	5.45
940	500 ppm	1.217	.244	1.21	4.28
910	500 ppm	1.258	.260	1.19	3.69
1000	0.5 %	1.062	.228	1.17	5.79
970	0.5%	1.117	.232	1.23	5.41
940	0.5%	1.221	.256	1.25	4.18
910	0.5%	1.247	.245	1.19	3.91
1000	5%	1.145	.226	1.26	5.42
970	5%	1.178	.245	1.23	4.61
940	5%	1.216	.235	1.18	4.32
910	5%	1.220	.247	1.24	4.30

* 100% O₂ flow

APPENDIX E

Effect of Sintering Temperature on the Densities and J_c Values

Densities and J_c Values for Sintering and Annealing
(450°C) in $\text{CO}_2 + \text{O}_2$ (Ambient Pressure) Gas Mixtures

Sintering Temperature (°C)	CO_2 Content	Relative Density (%)	J_c (A/cm ²)
1000	0 (100% O_2)	93	320
970	0 (100% O_2)	87	315
940	0 (100% O_2)	67	128
910	0 (100% O_2)	63	60
1000	50 ppm	92	157
970	50 ppm	86	138
940	50 ppm	67	21
910	50 ppm	62	0
1000	500 ppm	92	106
970	500 ppm	87	94
940	500 ppm	68	0
910	500 ppm	63	0
1000	0.5 %	92	81
970	0.5 %	86	0
940	0.5 %	66	0
910	0.5 %	62	0
1000	5 %	86	0
970	5 %	73	0
940	5 %	69	0
910	5 %	68	0