High Temperature Ceramic Superconductors: Oxalate Co-Precipitation Procedure for Synthesis and Influence of Compositional Variations

by

Mansour Ahmed Al-Shafei

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

April, 1990
INFORMATION TO USERS

This manuscript has been reproduced 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.
High temperature ceramic superconductors: Oxalate co-precipitation procedure for synthesis and influence of compositional variations

Al-Shafei, Mansour Ahmed, M.S.
King Fahd University of Petroleum and Minerals (Saudi Arabia), 1990
High Temperature Ceramic Superconductors: Oxalate Co-Precipitation Procedure for Synthesis and Influence of Compositional Variations

BY

MANSOUR AHMED AL-SHAFEI

A Thesis Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
in
CHEMISTRY

APRIL, 1990
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

COLLEGE OF GRADUATE STUDIES

This thesis, written by Mr. Mansour Ahmed Al-Shafei under the direction of his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMISTRY.

Thesis Committee

__________________________

M. S. Hussain
Thesis Advisor
(Prof. M. Sakhawat Hussain)

__________________________

Member (Prof. Mazhar-ul-Haque)

__________________________

A. Shafi Khattak
Member (Dr. Guldad Khattak)

__________________________

A. Somayaj
Department Chairman

__________________________

Dean, College of the Graduate Studies
ACKNOWLEDGEMENT

First and foremost thanks are to Allah for giving me the strength, patience and ability to accomplish this work.

I greatly owe my success to my parents, family, and friends for their Du’a’a and encouragement.

I wish to express my appreciation to my research advisor Professor M. Sakawat Hassain for his continuous cooperation, encouragement and guidance without which this work would not have been possible. I also wish to thank the other two members of my Thesis Committee, Professor Mazhar-ul-Haque and Dr. Guldad Khattak for their continuous help and for reviewing the thesis.

My thanks and appreciate are also due to Dr. Ahmad M. Bokhari, the previous Chairman of the KFUPM Chemistry Department, and Dr. Abdulaziz A. Al-Swayyan, the current Chairman of the Chemistry Department, for providing the facilities for completing this thesis.

I would also like to thank the Manager of Saudi Aramco’ Laboratories Department, Mr. Mughram Al-Houtan, Mr. Hafid Nagshhabandi, and Mr. AbdulElah Abu Al-Saud for giving me the opportunity to continue my study at KFUPM and for providing Saudi Aramco's facilities for completing this thesis.

Finally, I am thankful to Mr. Martin P. Sang, Mr. Jamil M. Bhatti and Dr. Vepan Keith for their assistance in acquisition of some of the data.
TABLE OF CONTENTS

List of tables
List of figures
Abstract
Dedication
Acknowledgement

Introduction

1.1: Superconductivity: A Chronological Account of Events 1
1.2: Development of Superconductivity in Ceramics 2

Literature review

2.1: Diagnostic Tests for Superconductivity 8
(a) Zero Resistance Effect 8
(b) Meissner Effect 9

2.2: Nomenclature for Ceramic Superconductors 10
2.3: Known High-T_c Ceramic Superconductors 10
2.4: X-Ray Structures of Ceramic Superconductors 11

2.4.1: Structure of Lanthanum-Copper Oxide Superconductor 12

2.4.2: Structure of Yttrium-Barium-Copper Oxides 13
(a) Structure of Tetragonal Form of Y-Ba-CuO 13
(b) Structure of Orthorhombic
form of Y-Ba-CuO

2.5: Procedures for Preparation Ceramic Superconductors
   2.5.1: Solid-State Pyrolysis Reactions
   2.5.2: Carbonate-hydroxycarbonate pyrolysis
   2.5.3: Oxalate Co-Precipitation Reaction

2.6: Effects of Compositional Variations
    on Superconductivity

2.7: Objectives of the present Thesis

Experimental Section

3.1: General preparation of superconducting materials
    using Oxalate-Coprecipitation procedure
    3.1.1: Preparation of a series of La(Ba/Sr/Ca)
           -CuO samples with variations in AE contents
    3.1.2: Preparation of (Y/Gd)-Ba-CuO series with
           variations in RE contents

3.2: Checks on Quality

3.3: Powder X-ray Diffraction (XRD) measurements
    (a) Sample Preparation
    (b) XRD Patterns

3.4: SEM and EDX Studies
    (a) Sample Preparation for SEM & EDX
        measurement
    (b) SEM Micrographs and EDX analysis
3.5: Levitation Experiments
3.6: Resistance versus Temperature Measurements
3.7: Reactivity

Results and discussion
4.1: Preparation by Oxalate-Co-precipitation Procedure
4.2: Comparative XRD and SEM Measurements on Superconducting and non-superconducting samples
4.3: Powder X-ray Diffraction (XRD) Studies
   (a) Results of XRD for La(Ba/Sr/Ca)-CuO Series
   (b) Results of XRD data for (Y/Gd)-Ba-CuO$_{7-\delta}$ series
4.4: Results of SEM and EDX Studies
   (a) Studies of La-(Ba/Sr/Ca)-CuO series
   (b) SEM Micrographs and EDX of (Gd/Y)-Ba-CuO series
4.5: Resistance versus Temperature Measurements
   (a) $T_C$ Measurements Of La-(Sr/Ba/Cu)-CuO Series having 21-Structure
   (b) $T_C$ Measurements Of (Y/Gd)Ba$_2$Cu$_3$O$_{7-\delta}$ having 123-Structure

Conclusions
References
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1</td>
<td>Superconductivity records through the years 1911-1988</td>
<td>3</td>
</tr>
<tr>
<td>Table 2-1</td>
<td>Known High-$T_C$ Ceramic Superconductors</td>
<td>11</td>
</tr>
<tr>
<td>Table 3-1</td>
<td>Stoichiometries of Samples A to Sample I for La-(Ba/Sr/Ca)-CuO series showing variations in AE contents</td>
<td>24</td>
</tr>
<tr>
<td>Table 3-2</td>
<td>Weight (gms) of reagent grade starting materials used to vary compositions in the La-(Ba/Sr/Ca)-CuO series</td>
<td>25</td>
</tr>
<tr>
<td>Table 3-3</td>
<td>Stoichiometries of Samples 1 to Sample 11 for the (Y/Gd)-Ba-CuO series showing variation in RE contents</td>
<td>26</td>
</tr>
<tr>
<td>Table 3-4</td>
<td>Weight (gms) of reagent grade starting materials used for each component to obtain (Y/Gd)-Ba-CuO series with different AE contents</td>
<td>27</td>
</tr>
<tr>
<td>Table 3-5</td>
<td>EDX analysis (Wt%) for copper, strontium and lanthanum in La-Sr-CuO system</td>
<td>69</td>
</tr>
</tbody>
</table>
Table 3-6: EDX analysis (Wt%) for yttrium, gadolinium, barium and copper

Table 3-7: Copper-constant thermal voltage

Table 4-1: Cell parameters for 123 structure samples annealed in oxygen atmosphere at 900°C

Table 4-2: Compositional variations and transition temperature data for the La-(Ba/Sr/Ca)-CuO series having 21-structure

Table 4-3: Composition variations and transition temperature data for (Y/Gd)-Ba-CuO series having 123-structure
LIST OF FIGURES

Figure 1-1: Highest known superconducting temperatures
Figure 2-1: Levitation of a cube of magnet over Y-Ba-CuO ceramic superconductor
Figure 2-2: Sketch for the La-Sr-CuO structure
Figure 2-3: Sketch of the orthorhombic phase and tetragonal phase Y-Ba-CuO
Figure 3-1: Room-temperature X-ray diffraction powder pattern for (A) Sample A :La$_{1.85}$Sr$_{0.15}$CuO$_4$ and Sample C: La$_{1.85}$(Sr=Ba=Ca=0.05)CuO$_4$
Figure 3-2: Room-temperature X-ray diffraction powder pattern for Sample B La$_{1.60}$Sr$_{0.40}$CuO$_4$
Figure 3-3: Room-temperature X-ray diffraction powder pattern for sample D: La$_{1.85}$Ba$_{0.15}$CuO$_4$
Figure 3-4: Room-temperature X-ray diffraction powder pattern for sample E: La$_{1.85}$(Sr=Ba=0.075)CuO$_4$
Figure 3-5: Room-temperature X-ray diffraction powder pattern for sample F: La$_{1.85}$(Sr=Ca=0.075)CuO$_4$
Figure 3-6: Room-temperature X-ray diffraction powder pattern for sample G: La$_{1.85}$(Ca=Ba=0.075)CuO$_4$
Figure 3-7: Room-temperature X-ray diffraction powder pattern for sample H: La$_{1.85}$Ca$_{0.15}$CuO$_4$
Figure 3-8: Room-temperature X-ray diffraction powder pattern for sample I: La$_{1.60}$Ca$_{0.40}$CuO$_4$
Figure 3-9: Room-temperature X-ray diffraction powder pattern for sample 1: \( \text{Y}_{1.0}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-10: Room-temperature X-ray diffraction powder pattern for sample 2: \( \text{Y}_{0.9}\text{Gd}_{0.1}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-11: Room-temperature X-ray diffraction powder pattern for sample 3: \( \text{Y}_{0.8}\text{Gd}_{0.2}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-12: Room-temperature X-ray diffraction powder pattern for sample 4: \( \text{Y}_{0.7}\text{Gd}_{0.3}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-13: Room-temperature X-ray diffraction powder pattern for sample 5: \( \text{Y}_{0.6}\text{Gd}_{0.4}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-14: Room-temperature X-ray diffraction powder pattern for sample 6: \( \text{Y}_{0.5}\text{Gd}_{0.5}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-15: Room-temperature X-ray diffraction powder pattern for sample 6: \( \text{Y}_{0.5}\text{Gd}_{0.5}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-16: Room-temperature X-ray diffraction powder pattern for sample 7: \( \text{Y}_{0.4}\text{Gd}_{0.6}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-17: Room-temperature X-ray diffraction powder pattern for sample 8: \( \text{Y}_{0.3}\text{Gd}_{0.7}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-18: Room-temperature X-ray diffraction powder pattern for sample 9: \( \text{Y}_{0.2}\text{Gd}_{0.8}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-19: Room-temperature X-ray diffraction powder pattern for sample 10: \( \text{Y}_{0.1}\text{Gd}_{0.9}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-20: Room-temperature X-ray diffraction powder pattern for sample 10: \( \text{Y}_{0.1}\text{Gd}_{0.9}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-21: Room-temperature X-ray diffraction powder pattern for sample 11: \( \text{Gd}_{1.0}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7} \)

Figure 3-22: Room-temperature X-ray diffraction powder pattern for \( \text{y(Gd}_{2}\text{O}_{2} \text{) for } \text{(A) Gd}_{2}\text{O}_{2} \text{ (B) Y}_{2}\text{O}_{3} \)}
Figure 3-23: Room-temperature X-ray diffraction powder pattern for (A) (COOH)\textsubscript{2}.2H\textsubscript{2}O (B) CuO

Figure 3-24: SEM micrograph for sample A : La\textsubscript{1.85}Sr\textsubscript{0.15}CuO\textsubscript{4}

Figure 3-25: SEM micrograph for sample D : La\textsubscript{1.85}Ba\textsubscript{0.15}CuO\textsubscript{4}

Figure 3-26: SEM micrograph for sample E : La\textsubscript{1.85}(Sr=Ba=0.075)CuO\textsubscript{4}

Figure 3-27: SEM micrograph for sample 1 : \textit{Y}_{1.0}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (first preparation)

Figure 3-28: SEM micrograph for sample 1 : \textit{Y}_{1.0}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (second preparation)

Figure 3-29: SEM micrograph for sample 2: \textit{Y}_{0.9}Gd\textsubscript{0.1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-30: SEM micrograph for sample 3: \textit{Y}_{0.8}Gd\textsubscript{0.2}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-31: SEM micrograph for sample 4: \textit{Y}_{0.7}Gd\textsubscript{0.3}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-32: SEM micrograph for sample 5: \textit{Y}_{0.6}Gd\textsubscript{0.4}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-33: SEM micrograph for sample 6 \textit{Y}_{0.5}Gd\textsubscript{0.5}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-34: SEM micrograph for sample 7: \textit{Y}_{0.4}Gd\textsubscript{0.6}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-35: SEM micrograph for sample 8: \textit{Y}_{0.3}Gd\textsubscript{0.7}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-36: SEM micrograph for sample 9: \textit{Y}_{0.2}Gd\textsubscript{0.8}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-37: SEM micrograph for sample 10: \textit{Y}_{0.1}Gd\textsubscript{0.9}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-38: SEM micrograph for sample 11: Gd\textsubscript{1.0}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

Figure 3-39: Photographed on a sample of \textit{Y}_{0.5}Gd\textsubscript{0.5}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}

showing levitation of a piece of magnet

Figure 3-40: Collinear four-probe array on a semi-infinite sheet

Figure 3-41: Schematic diagram for $T_c$ vs temperature measurements
Figure 3-42: Resistance vs temperature for 21 structure

Figure 3-43: Resistance vs temperature for sample 1: $Y_{1.0}Ba_{2}Cu_{3}O_{7}$

Figure 3-44: Resistance vs temperature for sample 2: $Y_{0.9}Gd_{0.1}Ba_{2}Cu_{3}O_{7}$

Figure 3-45: Resistance vs temperature for sample 3: $Y_{0.8}Gd_{0.2}Ba_{2}Cu_{3}O_{7}$

Figure 3-46: Resistance vs temperature for sample 4: $Y_{0.7}Gd_{0.3}Ba_{2}Cu_{3}O_{7}$

Figure 3-47: Resistance vs temperature for sample 5: $Y_{0.6}Gd_{0.4}Ba_{2}Cu_{3}O_{7}$

Figure 3-48: Resistance vs temperature for sample 6: $Y_{0.5}Gd_{0.5}Ba_{2}Cu_{3}O_{7}$

Figure 3-49: Resistance vs temperature for sample 7: $Y_{0.4}Gd_{0.6}Ba_{2}Cu_{3}O_{7}$

Figure 3-50: Resistance vs temperature for sample 8: $Y_{0.3}Gd_{0.7}Ba_{2}Cu_{3}O_{7}$

Figure 3-51: Resistance vs temperature for sample 9: $Y_{0.2}Gd_{0.8}Ba_{2}Cu_{3}O_{7}$

Figure 3-52: Resistance vs temperature for sample 10: $Y_{0.1}Gd_{0.9}Ba_{2}Cu_{3}O_{7}$

Figure 3-53: Resistance vs temperature for sample 11: $Gd_{1.0}Ba_{2}Cu_{3}O_{7}$

Figure 4-1: Loss of weight on cooling of sample from 860 °C to room temperature

Figure 4-2: Room-temperature X-ray diffraction powder pattern for non-superconductor sample 11: $Y_{0.0}Gd_{1.0}Ba_{2}Cu_{3}O_{7}$
Figure 4-3: Room-temperature X-ray diffraction powder pattern for non-superconducting sample 3 Y₀.₈Gd₀.₂Ba₂Cu₃O₇

Figure 4-4: Room-temperature X-ray diffraction powder pattern for non-superconducting sample 5 Y₀.₆Gd₀.₄Ba₂Cu₃O₇

Figure 4-5: Room-temperature X-ray diffraction powder pattern for non-superconducting sample 9 Y₀.₂Gd₀.₈Ba₂Cu₃O₇

Figure 4-6: Room-temperature X-ray diffraction powder pattern for sample 4: Y₀.₇Gd₀.₃Ba₂Cu₃O₇ at 2θ from 32.0° to 33.4°

Figure 4-7: Room-temperature X-ray diffraction powder pattern for sample 4: Y₀.₇Gd₀.₃Ba₂Cu₃O₇ at 2θ from 37.0° to 42.0°

Figure 4-8: Room-temperature X-ray diffraction powder pattern for sample 4: Y₀.₇Gd₀.₃Ba₂Cu₃O₇ at 2θ from 45.0° to 49.0°

Figure 4-9: Room-temperature X-ray diffraction powder pattern for sample 4: Y₀.₇Gd₀.₃Ba₂Cu₃O₇ at 2θ from 57.0° to 60.0°

Figure 4-10: SEM micrograph for sample 5: Y₀.₆Gd₀.₄Ba₂Cu₃O₇

Figure 4-11: XRD indexed pattern for sample 11: Gd₁.₀Ba₂Cu₃O₇

Figure 4-12: Variation of Tₐ with the intensity ratio (I₁/I₂) of the doublet around 32 to 33° of the Y-Ba-CuO system.

Figure 4-13: Resistance vs temperature for the following samples:
1: Y₁.₀Ba₂Cu₃O₇
2: Y₀.₉Gd₀.₁Ba₂Cu₃O₇
3: Y₀.₈Gd₀.₂Ba₂Cu₃O₇
4: Y₀.₇Gd₀.₃Ba₂Cu₃O₇
5: Y₀.₆Gd₀.₄Ba₂Cu₃O₇
Figure 4-14: Resistance vs temperature for the following samples:
6: $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_7$
7: $Y_{0.4}Gd_{0.6}Ba_2Cu_3O_7$
8: $Y_{0.3}Gd_{0.7}Ba_2Cu_3O_7$
9: $Y_{0.2}Gd_{0.8}Ba_2Cu_3O_7$
10: $Y_{0.1}Gd_{0.9}Ba_2Cu_3O_7$
11: $Gd_{1.0}Ba_2Cu_3O_7$
ملخص الرسالة

إن عدد الإبحاث التي تعقدت اكتشاف بدلورز وملر في عام 1966 لمادة الخزف على أنها مادة ما فوق المواد الموصولة في السنوات الاربع الماضية لانحسى في وقت قصير جدا لاميتها ولما يتوقع لها العلماء من تأثيرها في مجال التقنية الحديثة.

إذن هذه الإدراك كانت مدمجة على الخواص الفيزيائية والتركيبية البنائية والنظريات المتعلقة بخواص مادة الخزف نفسها.

ومع عظم هذه الإدراك فإنها لم تتطالب إلى حد بعيد دراسة دمج بعض العناصر الحاوية على نفس الصفات مع بعضها البعض أو تغيير تركيزها أو طرق انتاجها بطرق مختلفة عن الطرق التي انتجت بها عند اكتشافها. لقد تمت تجربة هذه المواد ببعون من الله عز وجل بطرق علمية معينة بعد تحسينها لكي تتوافق مع المواد التي استخدمت، علماً بأن هذه التفاعلات المشتركة علماً تتطلب نقاوة عالية جدا في المواد المستخدمة، ولم يكن هدف هذه الرسالة التوصل إلى مادة أو مواد مفاوقة الموصولة أعلى مما وصل إليها التقنية الحديثة.

وكان من أهداف هذه الرسالة أيضا اختبار هذه المواد ببحث الأساليب التقنية كاستخدام جهاز الميクロسكوب المعقد واختبار تركيز هذه المواد نقايا وتركيبها البنائي باستخدام الاعلى السينين وكذلك دراسة درجة الحرارة التي عندما تصبح هذه المواد مفاوقة الموصولة.

لقد تم تحضير أكثر من عشرين عينة من فئتين مختلفتين أحدهما احادية وثنائية التركيب والاخر احادية وثنائية وثلاثية التركيب من مادة الخزف وخمس عينات ليست موصولة ليتسمي دراسة الفرق بينها وبين المواد مفاوقة الموصولة.

لقد تم استبدال عنصر سترونيوم (Sr) بكل من عنصر الباريوم (Br) أو عنصر الكالسيوم (Ca) عند تحضير المادة الفيزيائية احادية التركيب وهي 4(Cu) اما بالنسبة للفئة الثانية فقد تم استبدال عنصر الباريوم (Y) بدلا من عنصر الجالودنيوم (Gd) حيث أن عدد الموالات بالنسبة للبترروم والجالودنيوم تكون مساوية واحدة وان قيم دلتا (δ) تكون بين خمسة من عشرة ونصف.
لقد استخدمت الأشعة السينية للتأكد من وجود التركيبة البنائية ذات النظام الرياضي السطوح في جميع عينات أحادي وثنائي التركيب، وكذلك العينات غير الموصلة من فئة أحادي وثنائي وثلاثي التركيب، كذلك استخدمت هذه الأشعة للتأكد من وجود التركيبة البنائية ذات النظام المعين المستقيم ذو ثلاثة محور متعامد غير متساوية في النظام من فئة أحادية وثنائية وثلاثية التركيب.

ولقد قمنا بقياس حجم البنورات التي تتكرر منها هذه العينات ووجدنا أنها تتراوح بين 0.15 - 10 جزء من مليون من المتر.

إن دراسة درجة الحرارة التي عندما تكون العينة موصلة للكهرباء أظهرت فكرة واضحة، إن عنصر الستريشيوم هو أفضل اليعادن عند مقارنته مع كل من عنصر الياريوم وعنصر كالسيوم بالنسبة للفئة أحادية وثنائية البنية وأن عنصر البتريوم (R) هو الأفضل عند مقارنته مع عنصر الجدولينيوم بالنسبة للفئة أحادية وثنائية وثلاثية البنية.
ABSTRACT

The extraordinary surge of scientific activity that followed the discovery of high-$T_C$ ceramic superconductors by Bednorz and Muller in 1986, led to an unprecedented number of publications in this area of research over a very short span of time. The research so far has primarily concentrated on aspects such as the unique physical properties of superconducting materials, structural characterization, theoretical models and development of these materials with still higher $T_C$. Relatively less attention has been paid to the dependence of superconducting properties on selective doping (or slightly off-stoichiometric compositional variations in the high-$T_C$ superconducting ceramics of known stoichiometries) as well as to the development of alternatives for solid-state pyrolysis procedures for the fabrication of these materials.

The objectives of the present thesis were mainly directed towards the development of new preparative procedures, rather than to prepare altogether new high-$T_C$ materials, and to study the effects of compositional variations using measurements such as X-ray Powder Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), and Resistance versus Temperature. Twenty-two superconducting samples of multi-component oxide having 21- and 123-structures, beside five non-superconducting samples, were prepared using oxalate co-precipitation method starting with reagent grade, rather than high-purity materials. A systematic substitution of Sr by Ba and/or Ca ions was carried out in the 21-structure ternary oxides having stoichiometry $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, to produce 4- and 5-component metal oxides of the $\text{La}_{1.85}\text{Sr}_{0.15-x}\text{AE}_x\text{CuO}_4$ series where $\text{AE} = \text{Ba}$ and/or $\text{Ca}$. 
Similarly, a systematic substitution of \( Y \) by \( \text{Gd} \) ions in 123-structures was carried out to produce 4- and 5-component metal oxides of the type \( Y_{1-x}\text{Gd}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) where \( 0<\delta<0.5 \). Similar procedure was used for all samples of both types of superconductors to generalize our preparation techniques. The conditions for co-precipitation, annealing, pulverization, effects of oxygen atmosphere, reaction with porcelain crucible and other processes were optimized for various compositions. X-ray powder diffraction (XRD) patterns confirmed the presence of a tetragonal phase in all \( \text{La-} (\text{Sr}/\text{Ba}/\text{Ca})\text{CuO} \) series and the non-superconducting RE-Ba-CuO samples. The presence of an orthorhombic phase was confirmed for all superconducting RE-Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) ceramic systems. Scanning Electron Microscopy (SEM) indicated the presence of grain sizes in the range of 0.3 to 15.0 \( \mu \text{m} \), while Energy Dispersive X-ray Spectroscopy (EDX) indicated the presence of La:AE ratio of 2:1 for \( \text{La-} (\text{Sr}/\text{Ba}/\text{Ca})\text{CuO} \) and 123 for \( \text{Y:Ba:Cu} \) for the \( \text{(Y/Gd)-Ba-CuO} \) series. The resistance versus temperature measurements indicate \( \text{Sr} \) being the best alkaline-earth metal among \( \text{Ca, Ba and Sr} \) for the ternary \( \text{La-containing ceramics} \) since substitution or doping of \( \text{Ca and/or Ba for Sr decreased the T}_c \) of these 21-structures. The resistance versus temperature data for 123-structures indicated that \( \text{Y} \) is the best choice among \( \text{Gd and Y} \) in the RE-Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) series. Substitution or doping of \( \text{Gd} \) for \( \text{Y} \) decreased the \( T_c \) to a lower value from 96K to about 91K.

The XRD, SEM, EDX and \( T_c \) measurements for both superconducting and non-superconducting samples are discussed with respect to the cell parameters, grain sizes, morphology, peak intensities, peak positions, single phase and/or multi-phase systems, transition temperature \( (T_c) \), transition width and \( T_c \) (onset). These characteristics
are further related to the compositional variation in the two series of samples studied.
This thesis is dedicated
to my parents, wife and my children Ahmed and Ali
CHAPTER 1
1: INTRODUCTION

The recent revolution\(^{(1-3)}\) in high temperature ceramic superconductors has generated intense research activity\(^{(4-6)}\) in the area of superconductivity because of important technological applications of superconductors and because the occurrence of superconductivity at high temperatures in ceramic materials was not expected. Based on a large volume of experimental information and theoretical understanding,\(^{(7)}\) the prevailing view prior to 1986, when high temperature superconductivity in oxides was discovered,\(^{(3-4)}\) was that the maximum value of the superconducting transition temperature \(T_C\) of any material would not exceed above 23K, the highest \(T_C\) recorded in 1973 for the compound Nb\(_3\)Ge.\(^{(8)}\) In fact, between 1911, the year H.K. Onnes discovered\(^{(9)}\) superconductivity in Hg, and 1986, \(T_C\) only increased at an average rate of about 0.25 K per year, but within the last three years (1986-1989) the maximum value of \(T_C\) has risen to about 125K in the new ceramics which were previously regarded as least likely candidates for high-\(T_C\) superconductivity due to having low concentration of charge carriers.

The research in superconducting phenomena has entered a breathtaking race in the last four to five years. These research efforts are mainly directed toward utilization of 95K Y-Ba-CuO material, on one hand, and to achieve yet higher-\(T_C\) materials, on the other. Studies dealing with X-ray structure determination, magnetic studies, materials development, oxygen stoichiometry, fabrication of thin films, and development of theoretical models for the high-\(T_C\) ceramic superconductors, have attracted attention of chemists, physicists, ceramists, all alike. Although a considerable amount of research has been carried out
to improve\(^{(10)}\) solid-state pyrolysis procedures for preparing ceramic superconductors, yet other synthetic procedures remained relatively underexplored. Similarly, systematic studies relating superconductivity with selective doping (or slightly off-stoichiometric compositional variations within a known high-\(T_C\) superconducting system) and correlation of \(T_C\) with physical measurements such as XRD and SEM of the doped materials, are not extensively carried out and further research is warranted on most of these aspects.

The present thesis deals with detailed investigation of oxalate coprecipitation procedure for preparing ceramic superconductors and an effort has been made to generalize this procedure for the synthesis of all types of ceramic superconductors. The \(T_C\) measurements of the two series of samples, prepared using oxalate-coprecipitation method, were carried out using the usual resistance versus temperature measurements. The samples were characterized using XRD & SEM measurements and the results were explained in terms of compositional variations in the parent sample of known stoichiometry.

1.1: Superconductivity: A Chronological Account of Events

The chronological development of superconductivity in metals, intermetallic compounds and ceramic materials since 1911 is summarized in Table 1.1. In 1908 H. Kamerlingh Onnes\(^{(9-10)}\) started the field of low-temperature physics by liquifying helium\(^{(4)}\) (He) in his laboratory in Leiden. Three years later he found that below 4.15K the dc resistance of mercury (Hg) dropped to zero. With the finding of "Resistanceless Current Flow" in metals at low temperatures the field of superconductivity was born. The next year Onnes discovered that the application of a sufficiently
strong axial magnetic field restored the resistance to its normal value.\(^{(11)}\) In 1913 the element lead (Pb) was found to be superconducting at 7.2K, and 17 more years were to pass before this record was surpassed by the element niobium (Nb) having \(T_C\) of 9.2K.

In 1933, another surprising characteristic of superconductivity was discovered by Meissner and Ochsenfeld.\(^{(12)}\) They found that a superconducting material will not permit a magnetic field to penetrate its bulk, a property that was later known as the Meissner effect. In the same year 1933,\(^{(12)}\) the isotope effect, whereby the transition temperature decreases when the average isotopic mass increases, was predicted theoretically by H. Frohlich\(^{(12)}\) and discovered experimentally by E. Maxwell and Coworkers.\(^{(13)}\)

Table 1.1: Superconductivity records through the years 1911-1988*

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>(T_C)(K)</th>
<th>Year of Discovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>Element</td>
<td>4.1</td>
<td>1911</td>
</tr>
<tr>
<td>Pb</td>
<td>Element</td>
<td>7.2</td>
<td>1913</td>
</tr>
<tr>
<td>Nb</td>
<td>Element</td>
<td>9.2</td>
<td>1930</td>
</tr>
<tr>
<td>Nb3Sn</td>
<td>Intermetallic</td>
<td>18.1</td>
<td>1954</td>
</tr>
<tr>
<td>Nb3Al0.75Ge0.25</td>
<td>Intermetallic</td>
<td>20-21</td>
<td>1966</td>
</tr>
<tr>
<td>Nb3Ga</td>
<td>Intermetallic</td>
<td>20.3</td>
<td>1971</td>
</tr>
<tr>
<td>Nb3Ge</td>
<td>Intermetallic</td>
<td>23.2</td>
<td>1973</td>
</tr>
<tr>
<td>Ba(<em>x)La(</em>{5-x})Cu5O(3-y)</td>
<td>Ceramic</td>
<td>30-35</td>
<td>1986</td>
</tr>
<tr>
<td>(La0.9Ba0.1)(_2)CuO(_4-d)</td>
<td>Ceramic</td>
<td>52.5</td>
<td>1986</td>
</tr>
<tr>
<td>YBa2Cu3O7-d</td>
<td>Ceramic</td>
<td>90-95</td>
<td>1987</td>
</tr>
<tr>
<td>BiSrCaCuO</td>
<td>Ceramic</td>
<td>105-120</td>
<td>1988</td>
</tr>
<tr>
<td>TlBaCaCuO</td>
<td>Ceramic</td>
<td>110-125</td>
<td>1988</td>
</tr>
</tbody>
</table>

* Data taken from Reference 11.
The Meissner effect provided support for the electron-phonon interaction, the "phonon mechanism" of superconductivity.\(^{(12)}\)

The two diagnostic tests of superconductivity, i.e., "Resistanceless Current Flow" and perfect diamagnetism or 'Meissner Effect' were appreciated only 50 years ago as having tremendous technological implications, but two major obstacles to implementing any new technology existed. First, extremely cold temperatures were required to achieve the superconducting state. Although liquid helium\(^{(4)}\) (He) could serve as a coolant, its scarcity and processing costs made it expensive; moreover, sophisticated equipment was required to handle it. The second problem was that the superconducting state of these elemental metals was easily destroyed by the application of modest external magnetic fields or electrical transport currents, making their use in electromagnetic applications impractical. These problems prompted an intensive search for new materials that would become superconducting at higher temperatures and remain superconducting in the presence of large magnetic fields and be able to support high current densities.

Scientists who studied this phenomenon dreamed of achieving superconductivity at or above 77K (-196°C), in which case liquid nitrogen (boiling point, 77K), which is cheap, easily handled, could be used as a coolant.

Alloys of niobium,\(^{(11)}\) particularly Nb-Ti, had been responsible for the greatest advances in superconductor technology. In 1973 the record for the transition temperature \(T_c\) was 23.3K for niobium germanium (Nb3Ge) thin films.\(^{(8)}\)
Another breakthrough\(^{(10)}\) involved the observation of superconductivity with certain organic salts, whose structures feature one-dimensional stacks of organic moieties that can be modified by chemical substitution. These salts also required temperatures in the range of liquid helium, to become superconducting. The fact that, while more than 20 metallic elements exhibit superconductivity, they all do so only at very low temperatures near that of liquid helium. Even compounds based on combining two or three elements required disappointingly low temperatures for superconductivity. Thus, the research activity for finding a material with yet a higher T\(_c\) remained active for all these years.

1.2: Development of Superconductivity in Ceramics

As recently as 1986, ceramic materials were not expected to show superconductivity. On April 17, 1986 the brief article "Possible High T\(_c\) Superconductivity in the Ba-La-CuO system", by J.G. Bednorz and K.A. Muller,\(^{(1)}\) published in Zeitschrift fur Physik received little attention until the Materials Research Society meeting in December 1986. There, the findings of Bednorz and Muller were substantiated by the University of Houston and the University of Alabama groups under Professor Paul Chu,\(^{(4)}\) M.K. Wu, Jr. and by a University of Tokyo group under the direction of Professors Kitazawa and Tanaka.\(^{(14)}\) The Tokyo group succeeded in making single phase samples of La\(_{2-x}\)Ba\(_x\)CuO\(_4\). The groups working at the University of Tokyo, the Institute of Physics in Beijing, ATT Bell Laboratories at Bell Communications Research, and IBM Zurich Laboratories had demonstrated that by substituting strontium (Sr) for barium (Ba) the transition temperature T\(_c\) could be raised to approximately 40K.\(^{(15-16)}\) The substitution of dipositive ions Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) for
tripositive La$^{3+}$ in the LaCuO$_4$ structure were indicative of the origin of superconductivity being a direct electronic mechanism rather than an ion size effect. Later the University of Houston group reported$^{(17)}$ that the application of high pressure (1.2 GPa) shifted the onset of the superconducting transition up to an astonishing 52K. Also, a number of groups reported$^{(17)}$ that the transition temperature was sensitive to the sintering and annealing atmospheres with the changes in T$_C$ related with the oxygen content. The changes were observed to be reversible down to the temperatures of at least 350°C.

The next dramatic breakthrough came with reports that superconductivity had been observed in polyphasic materials at temperatures above that of liquid nitrogen. The first announcement$^{(4)}$ in the USA was from the National Science Foundation on February 16th that Chu's group at the University of Houston had observed transition temperatures as high as 92K ($\sim$181°C). Later it became evident that a number of groups around the world, the Institute of Physics in Beijing$^{(19)}$, the Indian Institute of Science, Bangalore, had independently observed the same transition above liquid nitrogen temperatures in similar materials.$^{(19)}$ In all these cases, the investigators had substituted yttrium (Y) in place of lanthanum (La) in the La-Ba-CuO system to obtain the polyphasic superconducting material.

Immediately after the liquid nitrogen barrier had been broken, a race began to identify the superconducting phase and the structure responsible for the 90K range superconductivity. Figure 1.1 depicts the known highest-T$_C$ superconducting materials showing historical progression in T$_C$ of superconducting materials.
It has been published in High T_c Update\textsuperscript{(11)} that the Russian literature is more extensive than would be expected from an examination of the English language translation sources. For example, 62 reports were published in a special supplement of Pis'ma zh., representing two months' work in the USSR.

March 1988  125 K (-235°F)

February 1987  98 K (-283°F)

Nitrogen Liquifies at 77 K (-320°F)

New Oxide Compounds

April 1986  35 K (-397°F)

Mercury 1911

Figure 1-1: Highest known superconducting temperatures
CHAPTER 2
2: LITERATURE REVIEW

Relevant literature reviewing the detection, nomenclature, known high-$T_c$ materials and characterization of superconducting oxides is given below with respect to the following areas, which are specifically related to the present thesis.

(a) Diagnostic tests for superconductivity.
(b) Nomenclature of ceramic superconductors.
(c) Classes of known high-$T_c$ ceramic superconductors.
(d) Crystallographic structures of known ceramic superconductors.
(e) Procedures for preparation of ceramic superconductors.
(f) Effects of compositional variations on $T_c$.

2.1: Diagnostic Tests for Superconductivity

As mentioned earlier there are two main effects which are used in diagnostic tests for superconducting materials.

(a) Zero Resistance Effect

When materials become superconducting, all resistance disappears. In simplest terms, it is assumed that in superconductors the electrons are bound into pairs, which move in steps with each other avoiding collisions, allowing current to flow with no energy loss. This is contrary to the conductors, in which electrons are loosely bound and form a current when voltage is applied. The conductors have lower resistance which in turn is a measure of energy lost in the form of heat from electron collisions. In materials with extremely high resistance (insulators such as rubber or
glass) electrons are tightly bound to atoms and cannot be jostled loose to sustain a flow of current. The “Zero Resistance Effect” can be easily demonstrated by measuring resistance as a function of temperature. The temperature at which the resistance drops to zero is termed as "Transition Temperature" $T_c$, and the material is said to be superconducting at this temperature.

(b) Meissner Effect

This effect shows as flux expulsion in which the magnetic field is pushed completely out when the material becomes superconducting. Flux expulsion appears as a large negative susceptibility in the magnetic susceptibility measurements rendering the materials perfectly diamagnetic. Because of the Meissner Effect, a small permanent magnet floats above a superconductor with $T_c > 77$ K when the material is chilled to 77K in liquid nitrogen as shown below in Figure 2-1.

![Figure 2-1: Levitation of a cube of magnet over Y-Ba-CuO ceramic superconductor. The superconducting disk is bathed in liquid nitrogen.](image-url)
2.2: Nomenclature for Ceramic Superconductors

The two series of ceramic superconductors studied in the present thesis are derived from:

(a) lanthanum, strontium copper oxides, La$_{1.85}$Sr$_{0.15}$CuO$_{4-y}$, and (b) yttrium, barium copper oxides, YBa$_2$Cu$_3$O$_{7-x}$. These two types of superconductors differ from one another in (a) crystallographic structures, (b) transition temperatures which vary from 24 to 46K for La-Sr-CuO series and is in the region of 90K for Y-Ba-CuO series.

The structure of La-Sr-CuO superconductors (referred to as 21-Structure) is based on that of La$_2$CuO$_4$ compound with two La atoms for each Cu.$^{(20)}$ The Y-Ba-CuO superconductors have a structure based on the structure of YBa$_2$Cu$_3$O$_{7-x}$ with Y, Ba, Cu in the mole ratio of 1:2:3. This structure is referred to as 123-Structure.

2.3: Known High-$T_C$ Ceramic Superconductors.

All commonly known high-$T_C$ superconducting ceramics are listed in Table 2-1. One of the most striking aspects of all presently known high Tc ceramic superconductors with Tc greater than about 30K is that they are all copper oxides with layered perovskite-like crystal structure, all possessing CuO$_2$ planes. There are now something like two dozen high-$T_C$ superconducting ceramic materials with transition temperatures in the range of 90K to 125K. Experimental observations of increased $T_C$ up to 159K with temperature cycling in Y-Ba-CuO and Y-Ba-Cu(O/F) samples have been reported.$^{(21)}$ After these developments, the talk has been of finding materials that remain superconducting at $T_C$'s of 160K, 250K and beyond, as high as room temperature, but all these reports are dubious since none of these claims have been so far reconfirmed elsewhere, and the reproducibility
of these observations could not be demonstrated. Thus, so far no significant indications of room temperature superconductivity has been confirmed.(22)

Table 2-1: Known High-\(T_c\) Ceramic Superconductors

<table>
<thead>
<tr>
<th>Class</th>
<th>(T_c(\text{K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal, (La,Sr)(_2)CuO(_4)</td>
<td>35-40</td>
</tr>
<tr>
<td>Orthorhombic, YBa(_2)Cu(_3)O(_7-\delta)</td>
<td>90</td>
</tr>
<tr>
<td>Orthorhombic, Bi(_2)Sr(_2)CaCu(_2)O(_8)</td>
<td>85-110</td>
</tr>
<tr>
<td>Orthorhombic, Ti(_2)CaBa(_2)Cu(_2)O(_8)</td>
<td>125</td>
</tr>
<tr>
<td>Orthorhombic, Ti(<em>2)Ca(</em>{n-1})Ba(_2)Cu(_n-x)</td>
<td>125</td>
</tr>
<tr>
<td>New-type, Ln(_{2-x})Ce(<em>x)CuO(</em>{4-y})</td>
<td>24</td>
</tr>
</tbody>
</table>

2.4: X-Ray Structures of Ceramic Superconductors

In their first report on high-\(T_c\) superconductors, Bednorz and Muller\(^{(1)}\) referred to their samples as "metallic, oxygen deficient, perovskite-like mixed valent copper compounds". Subsequent X-ray and neutron diffraction studies confirmed that the new superconductors do indeed have characteristics of perovskite family.(23-25)

Perovskites characteristically have a ratio of two metal atoms for each three oxygen atoms. Some representative compounds with perovskite structure are CaTiO\(_3\) (Ca\(^{2+}\), Ti\(^{4+}\)), NaNbO\(_3\) (Na\(^+\), Nb\(^{5+}\)), LaAlO\(_3\) (La\(^{3+}\), Al\(^{3+}\)) and BaTiO\(_3\) (Ba\(^{2+}\), Ti\(^{4+}\)), in which the metal oxidation states sum up to +6\(^{(10)}\). There are different types of perovskite structures\(^{(23)}\). For example, above 200\(^\circ\)C bismuth titanate (BiTiO\(_3\)) is cubic (a=b=c) with a unit cell length of a = 4.0118Å and space group Pm\(_3\)m (Oh)\(^{(26)}\), at room
temperature it is tetragonal with unit cell dimensions $a=3.9947\text{Å}$, and $C=4.0336\text{Å}$; and below 5°C it is orthorhombic with unit cell dimension $a=5.669\text{Å}$, $b=5.682\text{Å}$ and $c=3.990\text{Å}$ with space group Amm2 ($C_{2v}$).

2.4.1: Structure of Lanthanum-Copper Oxide Superconductor

The ceramic systems $\text{La}_{1-x}\text{M}_x\text{CuO}_4$ with $\text{M}=\text{Sr}$ and $\text{Ba}$ are orthorhombic at low temperature and low $M$ contents,\(^{(27)}\) and tetragonal otherwise. Superconductivity has been observed on both sides of orthorhombic-tetragonal transition. The structure of $\text{La-Sr-CuO}$ can be described in terms of the compound $\text{La}_2\text{CuO}_4$, which is non-superconducting. When trivalent La ions are replaced by divalent cations such as Sr or Ba, the compounds become superconducting\(^{(18)}\). The tetragonal $\text{La-Sr-CuO}$ superconducting system has space group $I4/mmm$ $D_{4h}\(^{(20)}\)$ with copper atoms and one of the oxygen atoms located at special positions and all remaining atoms in general positions, with a single undetermined parameter associated with the $z$ coordinate. With $u=0.362$ and $v=0.182$, the typical lattice dimensions are $a=b=3.77\text{Å}$ and $c=13.18\text{Å}$. Figure 2-2 shows a sketch of the 21-structure of $\text{La-Sr-CuO}$ system.
2.4.2: Structure of Yttrium-Barium-Copper Oxides

The Y-Ba-CuO compounds like their La-Sr-CuO counterparts, also have tetragonal and orthorhombic phases. The orthorhombic phase is ordinarily superconducting. There are, however, some reported exceptions: (1) doping with gallium in copper chain sites can induce the orthorhombic-to-tetragonal transformation and the $T_C$ as high as 81K was observed, (2) replacing one oxygen by sulfur in EuBa$_2$Cu$_3$O$_7$ induces phase transformation with a small change in $T_C$ from 92 to 85K and (3) replacing one oxygen with two fluorines to form YBa$_2$Cu$_3$O$_5$F$_2$ produce a tetragonal phasic structure with all eight oxygen sites occupied and an enhanced $T_C$ was observed.

(a) Structure of Tetragonal Form of Y-Ba-CuO

The non-superconducting tetragonal form of YBa$_2$Cu$_3$O$_{7-\delta}$ with $\delta>0.5$, is stable above 650°C and has space group P4/mmm ($D_{4h}$) with one formula unit per unit cell. Yttrium and one copper atom are in special positions while all the remaining atoms are in general positions with a single undetermined parameter associated with the $z$ coordinate of each.
The unit cell dimensions of this phase are $a=3.9018\text{Å}$, $c=11.9403\text{Å}$, with slight variations reported by other investigators.\textsuperscript{(32)} The structure of this form is presented in Figure 2-3(b).

(b) Structure of Orthorhombic form of Y-Ba-CuO

Superconducting-orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$ having 123-structure has space group Pmmm (D$_{2h}$),\textsuperscript{(24-25)} with one formula unit per unit cell and representative lattice parameters are $a=3.827\text{Å}$, $b=3.882\text{Å}$, and $c=11.682\text{Å}$ with slight variations in these parameters reported by other investigators.\textsuperscript{(33)}

The orthorhombic form is sketched in Figure 2-3(a). It is clear that the oxygen site labelled as O(t) in tetragonal form is empty, resulting in cu-O(t')-Cu(t')-O- chains along the b direction.\textsuperscript{(34)} The vacancy of the O(t) site causes the unit cell to compress slightly along the 'a' rendering $a<b$. Orthorhombic phase of both Y-Ba-CuO and Gd-Ba-CuO are superconducting and were found to have space group Pmmm (D$_{2h}$).
Figure 2-3: Sketch of the orthorhombic phase (left) and tetragonal phase (right) Y-Ba-CuO, showing oxygen vacancy at O(t) site in the orthorhombic phase

2.5: Procedures for Preparation of Ceramic Superconductors

An enormous amount of materials research on high-$T_C$ superconductors has appeared since the report of Wu et al.\(^{(4)}\) for superconductors operating in liquid nitrogen with $T_C$ well above 90K (\(\approx -183^\circ\text{C}\)). The high-$T_C$ ceramics are generally obtained by a RE-AE-TM oxide combination using Rare-earth (RE) such as La, Y, Gd, alkaline earths (AE) such as Ba, Sr, Ca, and a transition metal (TM) such as Cu oxides. The ceramic materials have so far been prepared using one of the following general procedures.
2.5.1: Solid-State Pyrolysis Reactions

This is the most commonly used procedure for preparing superconducting ceramic materials. In this technique high purity oxygen-rich compounds such as oxides or carbonates of the desired metals (i.e., Ca, Sr, Ba, Bi, Y, Ti, Gd) are used as starting material. The steps involved in this procedure are given in Reaction Scheme I. The starting materials are mixed in the required mole ratios and ground to a fine powder to facilitate the calcination process which is carried out for approximately 20 hours at elevated temperatures (~900°C). This process is repeated several times, with intermittent pulverizing and mixing of partially calcined material at each step. As the reaction proceeds the color of the charge changes from green non-superconducting tetragonal phase to black superconducting orthorhombic phase. The process usually requires a final annealing in oxygen atmosphere followed by a slow cooling of the powder (or the pellets made from the powder) to room temperature. This procedure requires prolonged heating and very high purity starting materials. The presence of slight impurities usually result in biphasic tetragonal-orthorhombic mixture and complete superconductivity is not achieved.
2.5.2: Carbonate-hydroxycarbonate pyrolysis

This process involves co-precipitation of insoluble carbonates and hydroxycarbonates from a solution of the desired RE-AE-TM mixture, followed by sintering at elevated temperatures and pressure. The process is explained in Reaction Scheme II. This process has been used only in limited cases because high purity superconducting phase is only obtained after prolonged heat treatment of the mixture at elevated temperatures. Such a treatment is absolutely necessary for complete conversion of carbonates and hydroxycarbonates to ceramic oxides. In this procedure the
presence of slight traces of carbonate in the final ceramic material, usually result in biphasic material and complete superconductivity is not achieved.

Reaction scheme II: Carbonate-hydroxycarbonate co-precipitation procedure for preparing superconducting material.
2.5.3: Oxalate Co-Precipitation Reaction

In this process the materials for pyrolysis is obtained by co-precipitation of oxalates from a solution obtained by mixing individual solutions of nitrates, chlorides or carbonates of AE, RE and TM. This procedure does not require high purity starting material nor unusually prolonged heating and has several advantages over the other two procedures. The procedure has been modified and applied for preparing several samples in the course of the present research and a complete account is given in the experimental section.

2.6: Effects of Compositional Variations on Superconductivity

The effects of compositional variations have been generally investigated by other workers with the main objective of obtaining yet another higher-T_c ceramic material. Some of these studies involve:

(a) deviation from the ideal 1:2:3 composition in the case of Y-Ba-CuO system,
(b) substitution of other rare-earts (RE) for Y or La,\(^{(35)}\)
(c) replacement of transition metals by other than copper,\(^{(36-37)}\)
(d) replacement of alkaline earth (AE) by another AE,\(^{(38)}\) and
(e) substitution of group VI elements for oxygen,\(^{(39)}\)

Most of the above studies dealing with compositional variations involved replacement of one or more component in the La-Sr-CuO or Y-Ba-CuO systems, by another component of the same type. Studies dealing with doping of RE or AE in the known high-T_c material with
another AE or RE keeping the overall RE or AE contents the same, are not extensively reported in the literature.

2.7: Objectives of the present Thesis

The quest for higher-$T_C$ ceramics seems to be at a sticking point at the present moment. Improved processing techniques, doping or chemical substitution and other strategies do not appear to be effective in the direction of obtaining yet higher-$T_C$ superconductors. Our objectives in the present thesis are not specifically directed toward obtaining higher-$T_C$ materials but instead are aimed at:

(a) optimization and suitable modifications of oxalate co-precipitation route to prepare mixed RE-AE-CuO oxalate powders using reagent grade starting materials,
(b) application of the modified oxalate co-precipitation procedure to obtain a variety of high-$T_C$ materials, optimization of precipitation and calcination conditions which were observed to have strong impact upon key powder characteristics such as particle size, morphology, phase composition and microscopic homogeneity,
(c) systematic X-ray powder diffraction (XRD) studies showing the effects of compositional variations on the $T_C$'s of known superconducting ceramics, and
(d) SEM measurements of all representative samples to investigate their particle size, morphology and microstructures.

Consistent sets of XRD, SEM and $T_C$ data are not available on similar series of ceramics. Our efforts are directed toward obtaining complete set
of data for at least two series of sample. The following two multi-component oxide series were prepared and characterized using similar set of measurements.

**Series I:** Compositional changes in $\text{La}_{2-x}(\text{Sr/Ba/Ca})_x\text{CuO}_4$, $x=0.15$

Materials in this series display $T_c$ of about 35 K when Sr is the alkaline-earth used. Doping of Sr with Ba and/or Ca when La=1.85, is to be systematically carried out so that the total alkaline-earth contents remain equal to 0.15. A series of multi-component oxides is to be prepared with oxalate co-precipitation procedure using reagent grade starting materials. Influence of compositional variations on $T_c$'s is to be studied and characteristics of the new material are to be compared with the parent systems having $\text{La}=1.85$ and $\text{Sr}=0.15$.

**Series II:** Compositional changes in $(\text{Y/Gd})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

Influence of compositional variation of RE in the Y-Ba-CuO system having ideal 1:2:3 Y:Ba:Cu composition with $T_c$ around 90 K is to be studied. Yttrium-doping with Gd is to be carried out keeping the overall RE:AE:TM ratio equal to 1:2:3. A series of 4-component systems is to be prepared using oxalate co-precipitation procedure and $T_c$ measured as a function of compositional variation and annealing conditions under oxygen atmosphere.
CHAPTER 3
3: EXPERIMENTAL SECTION

3.1: General preparation of superconducting materials using Oxalate-Coprecipitation procedure.

All samples reported in this work were prepared by oxalate coprecipitation method using the following general procedure.

Stoichiometric quantities of the reagent grade RE oxides, AE carbonates and CuO were dissolved in 20-30 mL of concentrated nitric acid to obtain a clear blue to green solution. The solution was heated to dryness to remove NO₂ gas. The residue was then heated with 10% oxalic acid for complete precipitation of combined RE,AE & TM oxalates. The oxalate mixture was filtered under suction and dried overnight at about 80°C using alumina crucible with two intermediate grindings. The resulting black powder was vacuum, dried and then hydraulically pressed into pellets (1 cm diameter and 0.25 mm thick) under a pressure of about 20,000 psi. The general preparation steps are given in Reaction Scheme III.
Reaction Scheme III: Oxalates Co-Precipitation Procedure:

Reagent grade RE oxide and AE carbonates + CuO

**HNO_3** concentrated

Solution of nitrates

Filtration to remove residue, if any.

Heating with Oxalic acid

Light blue precipitation of mixed RE, AE & Cu oxalates

Centrifugation of the residue from the non-colored solution

Drying at 80°C for 10 hrs

Calcination at 860°C for 28 hrs with 3 intermediate grindings

Black powder of RE, AE & Cu oxides

Calcination at 900°C for 15 hrs with 2 intermediate grindings

Homogenous black powder

Pellets 1.0x0.25 cm at a pressure of 20,000 psi

Sintering at 900°C in oxygen atmosphere

Annealing at cooling rate of 25°C/15 min

Cooling to room temperature
3.1.1: Preparation of a series of La(Ba/Sr/Ca)-CuO samples with variations in AE contents

Nine samples of La-(Ba/Sr/Ca)-CuO series with compositions given in Table 3-1 were prepared using the oxalate-coprecipitation procedure described earlier.

Table 3-1: Stoichiometries of Samples A to Sample I for La-(Ba/Sr/Ca)-CuO series showing variations in AE contents

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>La$<em>{1.85}$Sr$</em>{0.15}$Cu$_{0.44}$ (Parent sample)</td>
</tr>
<tr>
<td>B</td>
<td>La$<em>{1.60}$Sr$</em>{0.40}$Cu$_{0.44}$</td>
</tr>
<tr>
<td>C</td>
<td>La$<em>{1.85}$(Sr=Ba=Ca=0.05)Cu$</em>{0.44}$</td>
</tr>
<tr>
<td>D</td>
<td>La$<em>{1.85}$Ba$</em>{0.15}$Cu$_{0.44}$</td>
</tr>
<tr>
<td>E</td>
<td>La$<em>{1.85}$(Sr=Ba=0.075)Cu$</em>{0.44}$</td>
</tr>
<tr>
<td>F</td>
<td>La$<em>{1.85}$(Sr=Ca=0.075)Cu$</em>{0.44}$</td>
</tr>
<tr>
<td>G</td>
<td>La$<em>{1.85}$(Ca=Ba=0.075)Cu$</em>{0.44}$</td>
</tr>
<tr>
<td>H</td>
<td>La$<em>{1.85}$Ca$</em>{0.15}$Cu$_{0.44}$</td>
</tr>
<tr>
<td>I</td>
<td>La$<em>{1.60}$Ca$</em>{0.40}$Cu$_{0.44}$</td>
</tr>
</tbody>
</table>

The starting materials for this series were reagent grade La$_2$O$_3$, SrCO$_3$, CaCO$_3$, BaCO$_3$ and CuO mixed in appropriate amount as given in Table 3-2.
Table 3-2: Weight (gms) of reagent grade starting materials used to vary compositions in the La-(Ba/Sr/Ca)-CuO series

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>La$_2$O$_3$</th>
<th>SrCO$_3$</th>
<th>CuO</th>
<th>BaCO$_3$</th>
<th>CuCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.0136</td>
<td>0.2215</td>
<td>0.7954</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.6604</td>
<td>0.5906</td>
<td>0.7954</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.0136</td>
<td>0.0738</td>
<td>0.7954</td>
<td>0.0987</td>
<td>0.0500</td>
</tr>
<tr>
<td>D</td>
<td>3.0136</td>
<td></td>
<td>0.7954</td>
<td>0.2960</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>3.0136</td>
<td>0.1107</td>
<td>0.7954</td>
<td></td>
<td>0.1480</td>
</tr>
<tr>
<td>F</td>
<td>3.0136</td>
<td>0.1107</td>
<td>0.7954</td>
<td></td>
<td>0.0751</td>
</tr>
<tr>
<td>G</td>
<td>3.0136</td>
<td></td>
<td>0.7954</td>
<td>0.1480</td>
<td>0.0751</td>
</tr>
<tr>
<td>H</td>
<td>3.0136</td>
<td></td>
<td>0.7954</td>
<td></td>
<td>0.1502</td>
</tr>
<tr>
<td>I</td>
<td>2.6064</td>
<td></td>
<td>0.7954</td>
<td></td>
<td>0.4004</td>
</tr>
</tbody>
</table>

The pellets obtained after heat treatment of oxalates were first sintered for 8-12 hours at 800-900°C, then pulverized into a homogeneous black powder and were sintered for another 8 hours at 800-900°C. The powder was compressed again into pellets at 30,000 psi, and the pellets were again sintered for 12 hours at 900°C, 2 hours at 1100°C and 6 hours at 900°C, and slowly cooled to 450°C at a cooling rate of 50°C/hour over a period of 8-10 hours, and finally brought to room temperature.
3.1.2: Preparation of (Y/Gd)-Ba-CuO series with variations in RE contents

Eleven samples of (Y/Gd)-Ba-CuO series having stoichiometries given in Table 3-3 were prepared during this work, again using oxalate co-precipitation procedure.

Table 3-3: Stoichiometries of Samples 1 to Sample 11 for the (Y/Gd)-Ba-CuO series showing variation in RE contents

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y₁.₀ Ba₂Cu₃O₇₋d (parent)</td>
</tr>
<tr>
<td>2</td>
<td>Y₀.₉Gd₀.₁Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>3</td>
<td>Y₀.₈Gd₀.₂Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>4</td>
<td>Y₀.₇Gd₀.₃Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>5</td>
<td>Y₀.₆Gd₀.₄Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>6</td>
<td>Y₀.₅Gd₀.₅Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>7</td>
<td>Y₀.₄Gd₀.₆Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>8</td>
<td>Y₀.₃Gd₀.₇Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>9</td>
<td>Y₀.₂Gd₀.₈Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>10</td>
<td>Y₀.₁Gd₀.₉Ba₂Cu₃O₇₋δ</td>
</tr>
<tr>
<td>11</td>
<td>Gd₁.₀Ba₂Cu₃O₇₋δ</td>
</tr>
</tbody>
</table>
Stoichiometric amount (as shown in Table 3-4) of the reagent grade Y$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$, and CuO obtained from Fluka Chemicals were dissolved separately in 10-40 mL dilute nitric acid.

Table 3-4: Weight (gms) of reagent grade starting materials used for each component to obtain (Y/Gd)-Ba-CuO series with different AE contents

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Stoichiometry</th>
<th>Y$_2$O$_3$</th>
<th>Gd$_2$O$_3$</th>
<th>BaCO$_3$</th>
<th>CuO</th>
<th>Oxalic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y$_{1.0}$Ba$_2$Cu$_3$O$_7$</td>
<td>1.1291</td>
<td></td>
<td>3.9470</td>
<td>2.3862</td>
<td>14.8132</td>
</tr>
<tr>
<td>2</td>
<td>Y$<em>{0.9}$Gd$</em>{0.1}$Ba$_2$Cu$_3$O$_7$</td>
<td>1.0162</td>
<td>0.1812</td>
<td>3.9470</td>
<td>2.3862</td>
<td>14.9059</td>
</tr>
<tr>
<td>3</td>
<td>Y$<em>{0.8}$Gd$</em>{0.2}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.9033</td>
<td>0.3625</td>
<td>3.9470</td>
<td>2.3862</td>
<td>14.9989</td>
</tr>
<tr>
<td>4</td>
<td>Y$<em>{0.7}$Gd$</em>{0.3}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.7904</td>
<td>0.5438</td>
<td>3.9370</td>
<td>2.3862</td>
<td>15.0917</td>
</tr>
<tr>
<td>5</td>
<td>Y$<em>{0.6}$Gd$</em>{0.4}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.6775</td>
<td>0.7250</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.1845</td>
</tr>
<tr>
<td>6</td>
<td>Y$<em>{0.5}$Gd$</em>{0.5}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.5645</td>
<td>0.9063</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.2795</td>
</tr>
<tr>
<td>7</td>
<td>Y$<em>{0.4}$Gd$</em>{0.6}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.4564</td>
<td>1.0875</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.3701</td>
</tr>
<tr>
<td>8</td>
<td>Y$<em>{0.3}$Gd$</em>{0.7}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.3387</td>
<td>1.2688</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.4629</td>
</tr>
<tr>
<td>9</td>
<td>Y$<em>{0.2}$Gd$</em>{0.8}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.2258</td>
<td>1.4500</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.5558</td>
</tr>
<tr>
<td>10</td>
<td>Y$<em>{0.1}$Gd$</em>{0.9}$Ba$_2$Cu$_3$O$_7$</td>
<td>0.1129</td>
<td>1.6312</td>
<td>3.9470</td>
<td>2.3862</td>
<td>15.6821</td>
</tr>
<tr>
<td>11</td>
<td>Gd$_{1.0}$Ba$_2$Cu$_3$O$_7$</td>
<td>1.8125</td>
<td>3.9470</td>
<td>2.3862</td>
<td></td>
<td>15.7423</td>
</tr>
</tbody>
</table>

The four solutions were mixed followed by filtration to obtain a clear solution.(40) An excess of 10% solution of oxalic acid was then added to obtain light blue precipitate of mixed oxalate. The precipitate was then centrifuged and dried at 80°C for 10 hours. The light blue powder was first fired for 28 hours at 860°C in air using an alumina crucible with three
intermediate grindings. During the heating procedure the color of the powder changed from green to black. The resulting black powder was then fired for 15 hours at 900°C in air with two intermediate grindings. The powder was then compressed into pellets (1.0 cm diameter and 0.25mm thick) under a pressure of about 20,000 psi using a hydraulic press. Often at this stage the material is deficient in oxygen, and is usually semi-conducting or sometimes even non-conducting. The pellets need to be sintered for at least 12 hours at 900°C in oxygen atmosphere and then cooled down at a cooling rate of 25°C/15 minutes over a period of 8-10 hours. Slow annealing under oxygen atmosphere from the elevated temperatures to room temperature is essential for producing the orthorhombic superconducting phase(40).

3.2: Checks on Quality

After the preparation of each sample, it was necessary to check its quality as a superconductor. All steps during the preparation were carefully monitored. More than 61 XRD, 60 SEM and 20 EDX were recorded to ensure the formation of the superconductor phase during the process. For example, XRD was done for representative samples after first, second, third and fourth day of heating at 860°C, in addition to, before and after annealing under oxygen at 900°C.

3.3: Powder X-ray Diffraction (XRD) measurements

(a) Sample Preparation

Each sample used for x-ray powder diffraction analysis (XRD) was ground to 200 mesh size in a porcelain mortar and pestle. About 1.5 g sample was cemented on top of an aluminum cylinder. The surface of the
specimen was pressed, scraped and excess powder was removed to form a flat surface. X-ray powder diffraction patterns were recorded at room temperature using a vertical Q-20 scanning PW-1700 Philips diffractometer. The diffractometer operating conditions were: normal fine - focus sealed-off Cu target x-ray tube, $\lambda=1.54060\text{Å}$, 45 K$\nu$, 40 mA, 6.00° take-off angle, 1° divergence slit, 0.2 mm receiving slit, graphite diffracted beam monochromator, rotating specimen, vacuum path, 35%-70% window, and 140° high angular limit. The diffractometer was calibrated using Si powder standard.

(b) XRD Patterns

The diffractograms for the nine samples of La-(Ba/Sr/Ca)-CuO series shown in Figures 3-1 to 3-8 and eleven samples of (Y/Gd)BaCuO series in Figures 3-9 to 3-21. The effects of reduced heating treatment on two representative samples (No. 6 and No. 10) as shown by XRD are depicted as Figures 3-14, 3-15, 3-19, and 3-20 while the XRD for the starting materials Gd$_2$O$_3$, Y$_2$O$_3$, CuO and oxalic acid, are included in Figures 3-22 and 3-23.
Figure 3-1 Room-temperature X-ray diffraction powder pattern for
(A) sample A: La1.85Sr0.15CuO4 (B) sample C: La1.85(Sr=Ba=Ca=0.05)CuO4
Figure 3-2 Room-temperature X-ray diffraction powder pattern for sample B: \( \text{La}_{1.60}\text{Sr}_{0.40}\text{CuO}_4 \) (A) before annealing (B) after annealing
Figure 3-3 Room-temperature X-ray diffraction powder pattern for sample D: La$_{1.85}$Ba$_{0.15}$CuO$_4$ (A) before annealing (B) after annealing
Figure 3-4 Room-temperature X-ray diffraction powder pattern for sample E: La_{1.85}(Sr=Ba=0.075)CuO_4 (A) before annealing (B) after annealing
Figure 3-5 Room-temperature X-ray diffraction powder pattern for sample F: La1.85(Sr=Ca=0.075)CuO4 (A) before annealing (B) after annealing
Figure 3-6 Room-temperature X-ray diffraction powder for sample G: La$_{1.85}$(Ca$_{0.025}$Ba$_{0.075}$)CuO$_4$ (A) before annealing (B) after annealing
Figure 3-7 Room-temperature X-ray diffraction powder pattern for sample H: La1.85Ca0.15CuO4 (A) before annealing (B) after annealing
Figure 3-8 Room-temperature X-ray diffraction powder pattern for sample I: La\textsubscript{1.60}Ca\textsubscript{0.40}CuO\textsubscript{4} (A) before annealing (B) after annealing
Figure 3-9 Room-temperature X-ray diffraction powder pattern for sample 1: Y1.0Ba2Cu3O7 (A) first time preparation (B) second time preparation
Figure 3-10 Room-temperature X-ray diffraction powder pattern for sample 2: Y0.9Gd1.0Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-11 Room-temperature X-ray diffraction powder pattern for sample 3: Y0.8Gd0.2Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-12 Room-temperature X-ray diffraction powder for sample 4: Y0.7Gd0.3Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-13 Room-temperature X-ray diffraction powder pattern for sample 5: Y0.6Gd0.4Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-14 Room-temperature X-ray diffraction powder pattern for sample 6: Y0.5Gd0.5Ba2Cu3O4 (A) after third day heating (B) after fourth day heating
Figure 3-15 Room-temperature X-ray diffraction powder pattern for sample 6: Y0.5Gd0.5Ba2Cu3O7 (A) after fifth day heating (B) after annealing
Figure 3-16 Room-temperature X-ray diffraction powder pattern for sample 7: Y0.4Gd0.6Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-17 Room-temperature X-ray diffraction powder for
sample 8: Y0.3Gd0.7Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-18 Room-temperature X-ray diffraction powder pattern for sample 9: Y0.2Gd0.8Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-19 Room-temperature X-ray diffraction powder pattern for sample 10: Y0.1Gd0.9Ba2Cu3O7 (A) after first day heating (B) after second day heating
Figure 3-20 Room-temperature X-ray diffraction powder pattern for
sample 10: Y0.1Gd0.9Ba2Cu3O7 (A) after third day heating (B) after annealing
Figure 3-21 Room-temperature X-ray diffraction powder for
sample 11: Gd1.0Ba2Cu3O7 (A) before annealing (B) after annealing
Figure 3-22 Room-temperature X-ray diffraction powder pattern for
(A) Gd2O3  (B) Y2O3
Figure 3-23 Room-temperature X-ray Diffraction pattern

for (A) (COOH)2.2H2O (B) CuO
3.4: SEM and EDX Studies

(a) Sample Preparation for SEM & EDX measurement

High-\( T_c \) superconductors are polycrystalline materials whose electrical, magnetic and mechanical properties are critically dependent on their chemistry and microstructures. In order to observe the grain size and the microstructure of a specimen, the scanning electron microscope (SEM) measurements were carried out on three representative samples of La-Sr-CuO systems and on all (Y/Gd)-BaCuO systems using JEOL JSM-35CF scanning electron microscope. Electrons from a filament under a pressure of about 10\(^{-5} \) torr were accelerated by a voltage in the range of \( \sim 25 \) Kv. The electron beam was demagnetized in the condenser lens and then focussed onto uncoated sample cemented in the sample holder by silver paste.

(b) SEM Micrographs and EDX analysis

SEM micrographs were taken at magnifications of X600, X4000 and X10000 and are shown in Figures 3-24 to 3-26 for La(Sr/Ba)CuO series and in Figures 3-27 to 3-38 for the (Y/Gd)-Ba-CuO series.
Figure 3-24: SEM micrograph for sample A: La1.85Sr0.15CuO4
Figure 3-25: SEM micrograph for sample D: La1.85Ba0.15CuO4
Figure 3-26: SEM micrograph for sample E: La1.85 (Sr=Ba0.075)CuO4
Figure 3-27: SEM micrograph for sample1: Y1.0Ba2Cu3O7
(First preparation)
Figure 3-28: SEM micrograph for sample1: Y1.0Ba2Cu3O7
(second preparation)
Figure 3-29: SEM micrograph for sample 2: Y0.9Gd0.1Ba2Cu3O7
Figure 3-30: SEM micrograph for sample3: Y0.8Gd0.2Ba2Cu3O7
Figure 3-31: SEM micrograph for sample 4: Y0.7Gd0.3Ba2Cu3O7
Figure 3-32: SEM micrograph for sample 5: Y0.6Gd0.4Ba2Cu3O7
Figure 3-33: SEM micrograph for sample 6: Y0.5Gd0.5Ba2Cu3O7
Figure 3-34: SEM micrograph for sample 7: Y0.4Gd0.6Ba2Cu3O7
Figure 3-35: SEM micrograph for sample 8: Y0.3Gd0.7Ba2Cu3O7
Figure 3-36: SEM micrograph for sample 9: Y0.2Gd0.8Ba2Cu3O7
Figure 3-37: SEM micrograph for sample 10: Y0.1Gd0.9Ba2Cu3O7
Figure 3-38: SEM micrograph for sample 11: Gd1.0Ba2Cu3O7
Chemical analyses with respect to yttrium, gadolinium, barium and copper were done by Energy Dispersive X-ray microanalysis (EDX) procedure using KEVEX MICRO-X7000 for the same samples (as used for SEM). The results of EDX are given in Table 3-5 for three samples in La-Sr-CuO series and in Table 3-6 for all samples in (Y/Gd)-Ba-CuO series.

Table 3-5: EDX analysis (Wt%) for copper, strontium and lanthanum in La-Sr-CuO system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements and Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>A</td>
<td>17.38</td>
</tr>
<tr>
<td>D (before annealing)</td>
<td>19.85</td>
</tr>
<tr>
<td>D (after annealing)</td>
<td>22.71</td>
</tr>
<tr>
<td>E (before annealing)</td>
<td>20.97</td>
</tr>
<tr>
<td>E (after annealing)</td>
<td>20.89</td>
</tr>
</tbody>
</table>

Compositions are
A = La$_{1.85}$Sr$_{0.15}$CuO$_4$
D = La$_{1.85}$Ba$_{0.15}$CuO$_4$
E = La$_{1.85}$ ((Sr=Ba=0.75)CuO$_4$)
Table 3-6: EDX analysis (Wt%) for yttrium, gadolinium, barium and copper

<table>
<thead>
<tr>
<th>Sample</th>
<th>Y</th>
<th>Gd</th>
<th>Ba</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.80</td>
<td>0.00</td>
<td>51.70</td>
<td>36.50</td>
</tr>
<tr>
<td>1-A</td>
<td>12.89</td>
<td>0.00</td>
<td>51.35</td>
<td>35.76</td>
</tr>
<tr>
<td>1-B</td>
<td>10.15</td>
<td>0.00</td>
<td>58.94</td>
<td>30.91</td>
</tr>
<tr>
<td>2</td>
<td>10.21</td>
<td>5.83</td>
<td>47.90</td>
<td>36.00</td>
</tr>
<tr>
<td>3</td>
<td>8.10</td>
<td>6.86</td>
<td>48.89</td>
<td>36.15</td>
</tr>
<tr>
<td>4</td>
<td>6.25</td>
<td>10.81</td>
<td>47.63</td>
<td>35.31</td>
</tr>
<tr>
<td>5</td>
<td>6.50</td>
<td>12.43</td>
<td>47.22</td>
<td>33.85</td>
</tr>
<tr>
<td>6</td>
<td>5.48</td>
<td>14.58</td>
<td>47.52</td>
<td>32.42</td>
</tr>
<tr>
<td>7</td>
<td>3.46</td>
<td>18.43</td>
<td>45.80</td>
<td>32.31</td>
</tr>
<tr>
<td>8</td>
<td>2.59</td>
<td>20.21</td>
<td>44.92</td>
<td>32.28</td>
</tr>
<tr>
<td>9</td>
<td>2.35</td>
<td>21.03</td>
<td>33.76</td>
<td>31.85</td>
</tr>
<tr>
<td>10</td>
<td>1.61</td>
<td>24.21</td>
<td>42.71</td>
<td>31.47</td>
</tr>
<tr>
<td>11</td>
<td>0.00</td>
<td>27.43</td>
<td>41.98</td>
<td>30.58</td>
</tr>
</tbody>
</table>

3.5: Levitation Experiments

A quick quality check for superconductivity was carried out by levitation experiment by cooling the sample in liquid nitrogen. Besides resistanceless current flow, the other diagnostic of a superconducting material is that it is perfectly diamagnetic.\(^{10}\) When the material becomes diamagnetic it will repel magnetic fields, a phenomenon called the Meissner
effect. Strong repulsive forces cause a very stable and quiet levitation, which apart from cooling, requires no energy input.(41)

Electromagnetism tells us that as the magnet approaches the pellet, it will induce a current in the surface of the superconductor.(10) Because the superconductor has no resistance, this current remains even after the magnet stops moving. It is a supercurrent. The supercurrent in turn induces a magnetic field. The induced magnetic field has just the right strength and geometry to cancel completely the effects of the magnetic field, arising from the magnet, in the bulk of the superconductor. Outside of the superconductor, however, the field caused by the magnet and the field induced by the superconductor repel one another, just as two north or two south poles of conventional magnets would. The result is that the magnet is suspended in limbo, its position dictated by the equilibrium between the downward gravitational force and the upward magnetic repulsive force, where the superconductor can be regarded as a kind of magnetic mirror.(10)

Levitation can be done when a pellet of the material is cooled in liquid nitrogen and a small magnet (1.5 x 8mm) is placed on the top of the pellet. If positioned carefully with plastic tweezers, the magnet will levitate in air above the superconductor,(42) as shown in Figure 3-39 for a sample prepared during the present study. This test was done on all samples before resistance was measured as a function of temperature. The bottom of a Styrofoam coffee cup was used as a liquid nitrogen container in which the pellets were cooled for a few minutes before suspending the permanent magnet.
Figure 3-39: Photographed on a sample of $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_7$ showing levitation of a piece of magnet.
3.6: Resistance versus Temperature Measurements

The collinear four-probe array, shown schematically in Figure 3-40 was used for the measurement of the resistance R of the material versus the temperature. This is the principal technique employed to determine when the material becomes superconducting (43). The transition temperature manifests itself by a sharp drop in resistivity to zero.

The electrical resistance measurements were performed on the annealed pellets. The contacts were made using pressed indium and the standard four-wire probe technique was used for measuring the resistance.

The resistance was measured over the temperature range 4.2-298K for La-(Ba/Sr/Ca)-CuO series and 40-160K in the case of Y(Gd)-Ba-CuO series starting with the sample immersed in liquid helium and then slowly brought to room temperature. The sample temperatures were determined by a calibrated germanium resistance thermometer imbedded in the copper block used for mounting the samples in the case of La-Ba-CuO and a thermocouple in the case of Y(Gd)-Ba-CuO series. The temperature-voltage relationship for the thermocouple is given in Table (3-7). The system assembled in the Physics Department for resistance vs temperature measurement is shown schematically in Figure (3-41).

The resistance vs temperature data was plotted using ICUSYS program on IBM 3033 computer of KFUPM-Data processing center.

The R vs T plots for La-(Ba/Sr/Ca)-CuO series is given in Figure (3-42). The curves for samples H and I are similar to A and D are not shown for the sake of clarity. The R vs T plots for eleven samples of (Y/Gd)-Ba-CuO series are shown in Figures (3-43) to (3-53) All the curves are indicative of superconducting samples with \( T_c \) varying with the change in composition.
### TABLE 3-7 COPPER-CONSTANT THERMALVOLTAGE

<table>
<thead>
<tr>
<th>T K</th>
<th>V µV</th>
<th>T K</th>
<th>V µV</th>
<th>T K</th>
<th>V µV</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>0.00</td>
<td>117</td>
<td>758.23</td>
<td>157</td>
<td>1719.86</td>
</tr>
<tr>
<td>78</td>
<td>16.32</td>
<td>118</td>
<td>779.84</td>
<td>158</td>
<td>1746.41</td>
</tr>
<tr>
<td>79</td>
<td>32.85</td>
<td>119</td>
<td>801.58</td>
<td>159</td>
<td>1773.08</td>
</tr>
<tr>
<td>80</td>
<td>49.47</td>
<td>120</td>
<td>823.45</td>
<td>160</td>
<td>1799.87</td>
</tr>
<tr>
<td>81</td>
<td>66.24</td>
<td>121</td>
<td>845.44</td>
<td>161</td>
<td>1826.78</td>
</tr>
<tr>
<td>82</td>
<td>83.14</td>
<td>122</td>
<td>867.56</td>
<td>162</td>
<td>1853.81</td>
</tr>
<tr>
<td>83</td>
<td>100.16</td>
<td>123</td>
<td>889.80</td>
<td>163</td>
<td>1880.96</td>
</tr>
<tr>
<td>84</td>
<td>117.35</td>
<td>124</td>
<td>912.17</td>
<td>164</td>
<td>1908.22</td>
</tr>
<tr>
<td>85</td>
<td>134.66</td>
<td>125</td>
<td>934.66</td>
<td>165</td>
<td>1935.60</td>
</tr>
<tr>
<td>86</td>
<td>152.19</td>
<td>126</td>
<td>957.28</td>
<td>166</td>
<td>1963.11</td>
</tr>
<tr>
<td>87</td>
<td>169.68</td>
<td>127</td>
<td>980.03</td>
<td>167</td>
<td>1990.72</td>
</tr>
<tr>
<td>88</td>
<td>187.39</td>
<td>128</td>
<td>1002.89</td>
<td>168</td>
<td>2018.16</td>
</tr>
<tr>
<td>89</td>
<td>205.24</td>
<td>129</td>
<td>1025.89</td>
<td>169</td>
<td>2046.01</td>
</tr>
<tr>
<td>90</td>
<td>223.22</td>
<td>130</td>
<td>1049.01</td>
<td>170</td>
<td>2074.28</td>
</tr>
<tr>
<td>91</td>
<td>241.33</td>
<td>131</td>
<td>1072.25</td>
<td>171</td>
<td>2102.37</td>
</tr>
<tr>
<td>92</td>
<td>259.58</td>
<td>132</td>
<td>1095.62</td>
<td>172</td>
<td>2130.57</td>
</tr>
<tr>
<td>93</td>
<td>277.96</td>
<td>133</td>
<td>1119.11</td>
<td>173</td>
<td>2158.89</td>
</tr>
<tr>
<td>94</td>
<td>296.47</td>
<td>134</td>
<td>1142.73</td>
<td>174</td>
<td>2187.32</td>
</tr>
<tr>
<td>95</td>
<td>315.12</td>
<td>135</td>
<td>1166.47</td>
<td>175</td>
<td>2215.84</td>
</tr>
<tr>
<td>96</td>
<td>333.89</td>
<td>136</td>
<td>1190.33</td>
<td>176</td>
<td>2244.54</td>
</tr>
<tr>
<td>97</td>
<td>352.80</td>
<td>137</td>
<td>1214.32</td>
<td>177</td>
<td>2273.31</td>
</tr>
<tr>
<td>98</td>
<td>371.84</td>
<td>138</td>
<td>1238.43</td>
<td>178</td>
<td>2302.21</td>
</tr>
<tr>
<td>99</td>
<td>391.01</td>
<td>139</td>
<td>1262.67</td>
<td>179</td>
<td>2331.21</td>
</tr>
<tr>
<td>100</td>
<td>410.32</td>
<td>140</td>
<td>1287.02</td>
<td>180</td>
<td>2389.57</td>
</tr>
<tr>
<td>101</td>
<td>429.75</td>
<td>141</td>
<td>1311.51</td>
<td>181</td>
<td>2389.57</td>
</tr>
<tr>
<td>102</td>
<td>449.31</td>
<td>142</td>
<td>1336.11</td>
<td>182</td>
<td>2416.92</td>
</tr>
<tr>
<td>103</td>
<td>469.01</td>
<td>143</td>
<td>1360.84</td>
<td>183</td>
<td>2448.36</td>
</tr>
<tr>
<td>104</td>
<td>488.83</td>
<td>144</td>
<td>1385.69</td>
<td>184</td>
<td>2477.96</td>
</tr>
<tr>
<td>105</td>
<td>508.78</td>
<td>145</td>
<td>1410.67</td>
<td>185</td>
<td>2507.65</td>
</tr>
<tr>
<td>106</td>
<td>528.87</td>
<td>146</td>
<td>1435.76</td>
<td>186</td>
<td>2537.45</td>
</tr>
<tr>
<td>107</td>
<td>549.08</td>
<td>147</td>
<td>1460.98</td>
<td>187</td>
<td>2567.36</td>
</tr>
<tr>
<td>108</td>
<td>569.42</td>
<td>148</td>
<td>1486.32</td>
<td>188</td>
<td>2597.39</td>
</tr>
<tr>
<td>109</td>
<td>589.88</td>
<td>149</td>
<td>1511.78</td>
<td>189</td>
<td>2627.53</td>
</tr>
<tr>
<td>110</td>
<td>610.48</td>
<td>150</td>
<td>1537.37</td>
<td>190</td>
<td>2657.78</td>
</tr>
<tr>
<td>111</td>
<td>631.21</td>
<td>151</td>
<td>1563.08</td>
<td>191</td>
<td>2688.14</td>
</tr>
<tr>
<td>112</td>
<td>652.06</td>
<td>152</td>
<td>1588.90</td>
<td>192</td>
<td>2718.62</td>
</tr>
<tr>
<td>113</td>
<td>673.04</td>
<td>153</td>
<td>1614.85</td>
<td>193</td>
<td>2749.21</td>
</tr>
<tr>
<td>114</td>
<td>694.14</td>
<td>154</td>
<td>1640.92</td>
<td>194</td>
<td>2779.90</td>
</tr>
<tr>
<td>115</td>
<td>715.38</td>
<td>155</td>
<td>1667.11</td>
<td>195</td>
<td>2810.71</td>
</tr>
<tr>
<td>116</td>
<td>736.74</td>
<td>156</td>
<td>1693.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-40  Collinear four-probe array on a semi-infinite sheet of thickness, d; outer probes 1 and 4 are the current input and output probes, inner probes 2 and 3 measure the potential difference, V, between them (43).
(1) Helium Dewar

(2) Sample Holder

(3) Digital Multimeter (3466A Hewlett Packard) for reading the resistance across the sample

(4) Digital Multimeter (Keithley) for measuring voltage across the sample.

(5) Current Source (225 Keithley Instruments)

(6) Nitrogen container

(7) Helium recovery

(8) Safety valve

Figure 3-41 Schematic diagram for Resistance vs temperature measurements
Figure 3-42 Resistance vs temperature for sample for 21 structure

Figure 3-43 Resistance vs temperature for sample 1: Y1.0Ba2Cu3O7
Figure 3-44 Resistance vs temperature for sample 2: Y0.9Gd0.1Ba2Cu3O7

Figure 3-45 Resistance vs temperature for sample 3: Y0.8Gd0.2Ba2Cu3O7
Figure 3-46 Resistance vs temperature for sample 4: Y0.7Gd0.3Ba2Cu3O7

Figure 3-47 Resistance vs temperature for sample 5: Y0.6Gd0.4Ba2Cu3O7
Figure 3-48 Resistance vs temperature for sample 6: Y0.5Gd0.5Ba2Cu3O7

Figure 3-49 Resistance vs temperature for sample 7: Y0.4Gd0.6Ba2Cu3O7
Figure 3-50 Resistance vs temperature for sample 8: Y0.3Gd0.7Ba2Cu3O7

Figure 3-51 Resistance vs temperature for sample 9: Y0.2Gd0.8Ba2Cu3O7
Figure 3-52 Resistance vs temperature for sample 10: Y0.1Gd0.9Ba2Cu3O7

Figure 3-53 Resistance vs temperature for sample 11: Gd1.0Ba2Cu3O7
3.7 Reactivity

The ceramics superconductors are not inert materials, but rather are sensitive to exposure to certain gases and to surface contact with particular materials. Great care must be exercised to avoid contamination from water vapor and carbon dioxide in the atmosphere.

In addition these materials are catalytic to oxygenation reactions, and these factors result in the occurrence of various chemical and other interactions, especially at elevated temperatures. The granular and porous nature of the materials has an accelerating affect on such reactions. Sample of Y-Ba-CuO may degrade in a matter of days when exposed to an ordinary ambient atmosphere; they react readily with liquid such as water, acids, and electrolytes, and moderately with basic solution. The reaction with water produces non-superconducting cuprates. The effects of acetone and other organics have been determined, and stable carboxyl groups have been found in the Y-Ba-CuO lattice. Hydrogen enters the Y-Ba-CuO lattice at elevated temperatures and forms a solid solution. Low concentrations have very little effect and high concentrations degrade the superconducting properties.
CHAPTER 4
4. RESULTS AND DISCUSSION

The results are discussed in terms of experimental techniques used and the effects of compositional variation in the two series of superconducting samples studied during this work.

4.1: Preparation by Oxalate-Co-precipitation Procedure

All samples were prepared using reagent grade starting materials and the experimental conditions for co-precipitation of oxalates, annealing, effects of oxygen atmosphere, reactions with porcelain crucible and pulverization processes were optimized for both series of superconducting copper oxide, and variations in compositions were studied. We observed that annealing for 6-12 hrs under oxygen atmosphere at 900°C of the compressed (ca. 30,000 psi) pellets of the black powder of (Y/Gd)-Ba-CuO series was necessary to obtain a superconducting material, because this treatment yields appropriate amount of oxygen in these metal oxides. At 600-1100K the Y-Ba-CuO system\(^{(48)}\) reversibly exchanges oxygen with the surroundings. This oxygen lost during the sample preparation effect lattice parameters \(a, b\) and \(c\) of Y-Ba-CuO system,\(^{(49)}\) in a regular manner even near the tetragonal to orthorhombic transformation temperature, which occurs between 620°C for 2% \(O_2\) and 700°C for 100% \(O_2\) in the furnace atmosphere.\(^{(50)}\) The amount of oxygen lost is entirely absorbed on cooling, provided that the cooling rate is not too fast and the sample is under enough oxygen pressure.\(^{(51)}\) Gallagher et al.,\(^{(52)}\) showed that the basic perovskite framework of cations was maintained for 7.0> \(x\)>6.0. However, the Y-Ba-CuO system could reversibly lose oxygen with
concomitant symmetry changes from orthorhombic Pmmn (x=7.0) to tetragonal P4/mmm (x=6.5) when heated above 500°C.

Figure (4-1) represents the weight lost during the heating procedure at 860°C for 28 hours, which reflects the weight lost in the conversion of the sample from tetragonal phase to orthorhombic phase. It has been reported\(^{51,53}\) that the tetragonal phase transforms into the orthorhombic when the sample annealed in air or in oxygen around 400-500°C, and 740°C at 1 atm oxygen.\(^{54}\)

![Graph showing weight loss vs. time](image)

**Figure 4-1:** Loss of weight on cooling of Sample from 860 °C to room temperature.

The experimental procedures such as the effect of heat treatment in air and under oxygen atmosphere, reproducibility of the procedure, reaction of porcelain crucible during heating were investigated as given below.

Firstly, conditions for heating treatment were optimized by changing the firing conditions. Instead of firing the sample at 850°C in air
with four intermediate grindings, Sample 11 (GdBa$_2$Cu$_3$O$_{7-\delta}$) was fired continuously at 900°C in air for 10 hrs without intermediate grindings, to see the effect of continuous heating on the crystal sizes, morphology, microstructure and resistance versus temperature data. The following were observed:

1. The resulting sample was not superconducting, showed no Meissner Effect, and remained unchanged even after subsequent heating for 28 hrs with intermediate grindings at 850°C.

2. The resulting sample was biphasic having the black superconducting as well as green nonsuperconducting phase.

3. The highest intensity XRD peak observed in the range of 30.0 to 35.0° for the corresponding superconducting sample (Figure 3-21B) was much reduced in intensity for the non-superconducting sample (Figure 4-2).

4. The XRD peaks at 32.0 to 33.0°, 46.0 to 47.0° and 57.5 to 59.5° in non-superconducting sample (Figure 4-2) were not split into doublets as is the case of superconducting sample (Figure 3-21B).

5. Several XRD peaks of almost equal intensities characteristic of tetragonal phase appeared in the range of 27.5 to 32° for non-superconducting sample (Figure 4-2). This XRD multiplet is always absent in the superconducting sample (Figure 3-21) and their presence is an indication of non-superconducting impurities.
From these observations it was concluded that the sample was composed of two phases having 121-structure and 123-structure, which may be due to insufficient oxygen in the atmosphere during the firing period, to convert the sample from the tetragonal to the orthorhombic phase. Thus, it was observed that preparation of a superconducting sample was very sensitive to the atmospheric conditions during the firing of the sample. The high-$T_c$ superconductors were usually obtained by repeated pulverizing and firing treatment of the mixed oxides$^{(55)}$. It has also been observed that having enough oxygen in the atmosphere was the key factor for preparing a superconducting sample$^{(56)}$ especially for the (Y/Gd)Ba$_2$Cu$_3$O$_{7-8}$ series.
Figure 4-2 Room-temperature X-ray diffraction powder pattern for non-superconductor sample 11: Gd1.0Ba2Cu3O7 showing the effect of continues heating without intermediate grinding.
Secondly, to ensure generality and reproducibility of the oxalate coprecipitation method, the same procedure was used for all samples in both series with several samples prepared in duplicate. For example, the superconducting Sample 1 (Y_{1.0}Ba_{2}Cu_{3}O_{7.5}) was prepared twice using similar preparation conditions. The XRD patterns (Figure 3-9) and SEM micrographs (Figures 3-27 and 3-28) of the two preparations agree with each other within the experimental errors. XRD pattern shows that the doublet ratio (I_1/I_2) of the peak in the range of 32.0 to 35.0° of the first preparation is 0.72 compared to 0.86 for the second preparation. The peaks in the range of 20.0 to 25.0°, 30.0 to 35.0°, 45.0 to 50.0° and 57.0 to 60.0° were all split into doublets, which is indicative of the presence of the superconducting orthorhombic phase. It was further clear from SEM micrographs (Figures 3-27 and 3-28) that both samples were homogeneously distributed having a connected path between the grains. The grain sizes were distributed between 2.0 - 3.5 mm. The fractures present in both samples are very common. It has been observed\(^{(56)}\) that a superconducting sample rich with yttrium has shown more fracture compared to other types of superconductors. Figures 3-27 and 3-28 at a magnification of 4000 revealed the sharpness of the grain boundaries of both samples. Some authors\(^{(57)}\) have suggested that superconducting phase exist on the surface or on the grain boundaries of a normal conducting material. Each grain\(^{(11)}\) of superconducting material contributes to lower the resistivity only if it links a connected path or contributed to a partial connectivity across the sample. SEM micrographs and XRD patterns agree that only one phase was present in the two samples. Quantitative analyses by energy dispersive X-ray (EDX) done for both samples using standardless method, confirmed the absence of all elements other than Y,
Ba and Cu. The weight percent of Y, Ba and Cu is 11.8%, 51.7% and 36.5% in the first sample, and 12.89%, 51.35 and 35.76% in the second sample (Table 3-6).

Thirdly, to ensure the reaction of RE-AE-TM oxides at higher temperatures with the porcelain crucible used for heating the mixed metal copper oxide superconductors, three different samples: Sample 3 (Y$_{0.8}$Gd$_{0.2}$Ba$_2$Cu$_3$O$_{7-\delta}$) Sample 5 (Y$_{0.6}$Gd$_{0.4}$Ba$_2$Cu$_3$O$_{7-\delta}$) and Sample 9 (Y$_{0.2}$Gd$_{0.8}$Ba$_2$Cu$_3$O$_{7-\delta}$) were prepared by using porcelain crucible instead of alumina crucible. The resulting ceramic materials were not superconductors and all the samples were observed to be contaminated with BaAl$_2$O$_4$ as detected by XRD analyses and shown in Figure 4-3 to 4-5. An intense peak appearing at about 28° clearly matched the strongest peak in the BaAl$_2$O$_4$ standard. These XRD revealed that porcelain crucibles are not suitable for preparing superconducting materials. Our observations were in agreement with the report of Ishii et al.\(^{(58)}\) who prepared a superconducting YBa$_2$Cu$_3$O$_7$ films using an aluminum plate with the tape casing method, and reported BaAl$_2$O$_4$ contamination in the films which were sintered at 950°C. These films were not superconductors and BaAl$_2$O$_4$ crystals were detected in the sample. Our XRD studies of porcelain contaminated samples revealed the presence of BaAl$_2$O$_4$ peaks around 27.0 to 30.0°, 32.0 to 35.0°, 40.0 to 42.0° and 56.0 to 59.0° in all the samples. Besides BaAl$_2$O$_4$ peaks at 32.0 to 34.0° there was a peak belonging to Y$_2$O$_3$ which may have formed as a result of the presence of BaAl$_2$O$_4$ in the material. To confirm that the reagent grade starting materials were not contaminated with BaAl$_2$O$_4$ (Figures 3-22 and 3-23) represents XRD patterns for the starting materials, Y$_2$O$_3$ and Gd$_2$O$_3$. 
Figure 4-3 Room-temperature X-ray diffraction powder pattern for (non-superconducting) sample 3 Y0.8Gd0.2Ba2Cu3O7
Figure 4-4: Room-temperature X-ray diffraction powder pattern for (non-superconducting) sample 5 Y0.6Gd0.4Ba2Cu3O7
Figure 4-5: Room-temperature X-ray diffraction powder pattern for (non-superconducting) sample 9 Y0.2Gd0.8Ba2Cu3O7
XRD patterns exhibited nearly identical peaks in the range of 20.0 to 50.0°, but for the range between 50.0 to 60.0°, the number of peaks in Y₂O₃ were more as compared to Gd₂O₃. Most of the peaks appearing in the XRD spectra of the starting materials i.e. Y₂O₃ and Gd₂O₃, disappeared completely on the formation of the superconducting materials, specially the peak in the range of 27.0 to 30.0°.

On the basis of the above preparative procedures and XRD/SEM measurements carried out during the fabrication of the two series of superconducting samples, it could be concluded that oxalate-co-precipitation technique has several advantages over the other procedures, specifically over the commonly used solid-state pyrolysis method. Some of these advantages are due to the fact that the oxalate co-precipitation procedure provides:

(a) smaller grain size through controlled precipitation of mixed oxalates,
(b) better homogeneity and mixing of starting materials in solution state,
(c) ease of conversion of oxalates (than carbonates) to oxides,
(d) reagent grade starting materials rather than high purity materials requirement,
(e) annealing under oxygen atmosphere being not absolutely necessary at least for La-(Ba/Sr/Ca)-CuO series,
(f) better stoichiometric ratios, and
(g) high reproducibility and general applicability over a wide variety of samples of 12- and 123-structures.
While using oxalate co-precipitation for preparing superconducting material, the following should be carefully observed:

(a) porcelain crucible is not suitable during firing process,
(b) intermediate grinding at least twice during the first 12 hours of firing and pelletization is necessary,
(c) annealing under oxygen atmosphere and slow cooling rate is required for (Y/Gd)-Ba-CuO series while oxygen annealing is not absolutely necessary for La-(Sr/Ba/Ca)-CuO series.

4.2: Comparative XRD and SEM Measurements on Superconducting and non-superconducting Samples

To detect the differences in XRD peak positions, shapes and intensities, microstructure(s), grain sizes and grain growth, XRD patterns and SEM micrographs were obtained for a superconducting as well as for the corresponding non-superconducting samples. Two samples having the same composition \((Y_{0.7}Gd_{0.3}Ba_2Cu_3O_{7-\delta})\) except that one of the samples showed Meissner effect (i.e., levitation) while the other did not exhibit any levitation were used for the comparative studies. The XRD patterns for both the orthorhombic (superconducting) and the tetragonal (non-superconducting) samples were quite similar except that the intensities and shapes of some peaks were different. The intensity ratio of four doublets around 32.0 to 33.5°, 37.0 to 42.0°, 45.0 to 49.0° and 57.0 to 60.0° in the XRD spectra (Figures 4-6 to 4-9), were found to be reversed in the superconducting samples as compared to the non-superconducting sample.
Figure 4-6 Room-temperature X-ray diffraction powder pattern for

(A) sample 4: Y0.7Gd0.3Ba2Cu3O7 (orthorhombic)

(B) sample 4: Y0.7Gd0.3Ba2Cu3O7 (tetragonal)
Figure 4-7 Room-temperature X-ray diffraction powder pattern for

(A) sample 4: Y0.7Gd0.3Ba2Cu3O7 (orthorhombic)

(B) sample 4: Y0.7Gd0.3Ba2Cu3O7 (tetragonal)
Figure 4-8 Room-temperature X-ray diffraction powder pattern for

(A) sample 4: $\text{Y}0.7\text{Gd0.3Ba2Cu3O7}$ (orthorhombic)

(B) sample 4: $\text{Y}0.7\text{Gd0.3Ba2Cu3O7}$ (tetragonal)
Figure 4-9 Room-temperature X-ray diffraction powder pattern for

(A) sample 4: Y0.7Gd0.3Ba2Cu3O7 (orthorhombic)
(B) sample 4: Y0.7Gd0.3Ba2Cu3O7 (tetragonal)
This reversal in peak shape is a diagnostic difference between the non-superconducting (tetragonal) phase and the corresponding superconducting (orthorhombic) phase. There are several reasons for explaining why the sample became non-superconductors:

(1) There was not enough atmospheric oxygen during the heating process used in preparation of the samples for exchanging the oxygen lost from the material during heating.\(^{(7)}\)

(2) Cooling rate was too rapid for the samples after annealing not allowing re-absorption of enough oxygen. Since the conversion from tetragonal to orthorhombic take place during the cooling process, the sample remained non-superconducting.\(^{(11)}\)

(3) Annealing time of 6-12 hrs at 900°C of the compressed (ca. 30,000 psi) pellet of the black powder was not enough for the sample.
The SEM micrographs (Figure 4-10), also revealed no significant differences between the superconducting and the non-superconducting samples, except bigger grain size for the later. The overall grain size is 2.0 \( \mu m \) in the case of non-superconductor samples whereas it is 8.0 \( \mu m \) in the superconducting sample. At the magnification of 4000, this difference appears quite clearly, where the grains overlap with each other and form a channel between them.

Table (3-6) presents the quantitative analyses of the superconducting sample and the non-superconducting sample. It is clear that there was a shortage of Cu contents in the non-superconducting sample by 15.3% compared to the superconducting sample. This reflects that Cu was not distributed enough over both the CuO planes and the chains\(^{(59)}\).

This also supports the belief that\(^{(35)}\) copper is involved directly in superconductivity while La, Ba and Y are not. In the LaSrCuO system substitution for the copper ions have a much more drastic effect on the superconductivity than substitution for lanthanum or an alkali metal ion.\(^{(11)}\) This stresses the importance of the Cu-O-Cu-O linkages.\(^{(35)}\) Cations such as \( \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Y}^{3+} \) and \( \text{La}^{3+} \) present in oxide superconductors have definite valence states, as does \( \text{O}^{2-} \). The charge states \( \text{Cu}^{+} \) and \( \text{Cu}^{2+} \) are quite common in chemical compounds and crystals, while \( \text{Cu}^{3+} \) is rare. Average copper valence obtained in a crystallographic study of \( \text{YBaCuO}^{(11)} \) over a range of temperature from 20 to 750\(^{\circ}\) showed that one \( \text{Cu}^{3+} \) and two \( \text{Cu}^{2+} \) atoms of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) are distributed over both the CuO planes and the chains, with somewhat more \( \text{Cu}^{3+} \) in the chains. Some authors\(^{(60)}\) have suggested that divalent copper can participate in the charge interchange \( 2\text{Cu}^{2+} \rightarrow \text{Cu}^{+} + \text{Cu}^{3+} \).
Figure 4-10: SEM micrograph for sample 5: Y0.6Gd0.4Ba2Cu3O7
Of course, other possibilities also exist. For example, it has been proposed(61) that charge fluctuations might occur between Cu$^{2+}$O$^2$ and Cu$^{+}$O$^-$ in the CuO$_2$ planes of YBa$_2$Cu$_3$O$_7$. Charge transfer could also take place between Cu$^+$ and Cu$^{2+}$ or between Cu$^{2+}$ and Cu$^{3+}$.(62)

4.3: Powder X-ray Diffraction (XRD) Studies:

Both series were quite extensively investigated using XRD and the results are separately discussed for the two series.

(a) Results of XRD for La(Ba/Sr/Ca)-CuO Series

In the case La(Ba/Sr/Ca)CuO samples having 21-structure, XRD patterns (Figures 3-1 to 3-8) revealed almost identical line positions before and after annealing and no direct relation between the peak intensity ratios of samples before and after annealing were observed for the XRD peaks in the range of 30.0 to 35.0°. The intensity ratio ($I_1/I_2$) of Sample E (La$_{1.85}$(Sr=Ba=0.75)CuO$_4$) observed in Figure 3-4 decreases while the reverse took place in the case of Sample D (La$_{1.85}$Ba$_{0.15}$CuO$_4$) as shown in Figure 3-3 on changing the AE contents from Sr=0.075/Ba=0.075 in Sample E to Ba=0.15 in Sample D, while keeping all other components constant.

From the ionic radii(11) (Ba$^{2+} = 1.34\text{Å}$, and Sr$^{2+} = 1.12\text{Å}$), one could estimate that a replacement of Ba$^{2+}$ which has bigger radius by Sr$^{2+}$ effect the CuO$_2$ layers which has a relation with $T_c$ measurement.
Annealing the compressed pellet of the black powder for 6-9 hrs at 900°C dramatically affect the peak intensities and shape of Samples A, B and I in La(Ba/Sr/Ca)-CuO series (Figures 3-1, 3-2 and 3-8). It is interesting to note that the peak at 25.0 to 30.0°, which split into triplets reversed in shape after annealing, which is not the case in the rest of the samples in the 21-structure system. The group of XRD peaks at 37.0 to 40.0°, 47.0 to 50.0°, and 52.0 to 55.0° increased in intensities after annealing but no shape reversal was observed. There were three peaks in the range of 22.0 to 27.0° in Sample B before annealing, but after annealing, the intensity of the first peak increased, and the other two peaks disappeared completely. XRD patterns of Samples D, E, F, G and H show that the peaks were reversed, increased in intensities, and all minor peaks completely disappeared after the samples were annealed. Sintering mechanism was of practical importance because it was the best way to control the development of microstructure.\(^{(63)}\)

(b) Results of XRD data for (Y/Gd)-Ba-CuO\(_{7.8}\) series.

The XRD patterns (Figures 3-9 to 3-21) of (Y/Gd)-Ba-CuO series having 123-structure prepared during the course of this work, were used not only in identifying the phase(s) present in each sample, but also in testing for any contamination in the sample. The XRD spectra were used for measuring the cell parameters given in Table 4-1 and based upon indexing shown in Figure 4-11.

Sample 10 (Y\(_{0.1}\)Gd\(_{0.9}\)Ba\(_2\)Cu\(_3\)O\(_7\)) was analyzed after heating for 7 hrs at 860°C. The sample at this stage was biphasic having both the tetragonal and the orthorhombic phases, but as more heating was
Figure 4-11: XRD indexed pattern for sample 1: Gd1.0Ba2Cu3O7
applied, the orthorhombic phase of (Y0.1Gd0.9Ba2Cu3O7) increased with a decrease in the other phase as shown in Figures 3-19 and 3-20).

XRD pattern (Figure 3-10) of Sample 2 (Y0.9Gd0.1Ba2Cu3O7) shows that the intensity of all the peaks increased after annealing for 12 hrs in oxygen atmosphere. The peak intensity at 23.0° increased more than twice after annealing. The two peaks in the range of 37.0 to 42.0° increased and also reversed in shape. The peak at 47.0° appeared as a doublet with intensity ratio of (I1/I2 = 0.72) before annealing and 0.28 after annealing.

Table 4-1: Cell parameters for 123 structure samples annealed in oxygen atmosphere at 900°C

<table>
<thead>
<tr>
<th></th>
<th>a Å</th>
<th>b Å</th>
<th>c Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.8276</td>
<td>3.8934</td>
<td>11.6651</td>
</tr>
<tr>
<td>2</td>
<td>3.7126</td>
<td>3.8766</td>
<td>11.5811</td>
</tr>
<tr>
<td>3</td>
<td>3.4269</td>
<td>3.8929</td>
<td>11.6728</td>
</tr>
<tr>
<td>4</td>
<td>3.8766</td>
<td>3.9372</td>
<td>11.5811</td>
</tr>
<tr>
<td>5</td>
<td>3.8284</td>
<td>3.8934</td>
<td>11.669</td>
</tr>
<tr>
<td>6</td>
<td>3.8309</td>
<td>3.8929</td>
<td>11.6844</td>
</tr>
<tr>
<td>7</td>
<td>3.8366</td>
<td>3.8934</td>
<td>11.6651</td>
</tr>
<tr>
<td>8</td>
<td>3.6766</td>
<td>3.8808</td>
<td>11.5849</td>
</tr>
<tr>
<td>9</td>
<td>3.8971</td>
<td>3.9167</td>
<td>11.6651</td>
</tr>
<tr>
<td>10</td>
<td>3.7198</td>
<td>3.8925</td>
<td>11.6998</td>
</tr>
<tr>
<td>11</td>
<td>3.6392</td>
<td>3.8720</td>
<td>11.5171</td>
</tr>
<tr>
<td>*</td>
<td>3.831</td>
<td>3.881</td>
<td>11.651</td>
</tr>
</tbody>
</table>

*This data was taken from Reference (11) for YBa2Cu3O7-δ sample.

The XRD of Sample 2 (Figure 3-10) shows that the peak at 23.0° decreased in intensity after annealing. Moreover, the two peaks in the
range of 37.0 to 42.0° decreased in intensity after annealing without reversal in their shapes. Also some very small peaks between 27.00 to 30.0° disappeared after annealing.

Sample 4 XRD pattern (Figure 3-12) revealed insignificant differences in peak intensity or shape after annealing.

XRD pattern of Sample 5 (Figure 3-13) showed an enormous increase in the peak intensity at 23.0° after annealing compared to all the peaks at the same position in all the 123 structure system. The two peaks in the range of 37.0 to 42.0° differed in intensity from I₁/I₂=1.0 before annealing to 0.28 after annealing.

XRD patterns of Sample 6 (Figures 3-14 and 3-15) revealed no change in the peak position after second day heating (14 hrs with two intermediate grindings), third day heating (21 hrs with three intermediate grindings), fourth day (28 hrs with four intermediate grinding) at 860°C, and after annealing in oxygen atmosphere at 900°C, except that a small peak in the range of 27.0 to 32.0° disappeared after annealing.

Sample 7 XRD pattern (Figure 3-16) exhibited only minor changes in the peak intensities without any change in the peak positions.

XRD pattern for Samples 8, 9 and 11 (Figures 3-17, 3-18, and 3-20) showed a reversal in peak shapes around 37.0 to 43.0° after annealing.

XRD pattern of Sample 10 (Figures 3-19 and 3-20) showed the phase(s) present in the sample after first day heating, second day heating, fourth day heating and also after annealing.

Heating and grindings are very important processes for having a monophasic superconducting samples. As more heating at 860°C was applied the material lost oxygen to the surrounding atmosphere, and changed from tetragonal P4/mmm (δ>0.5) to orthorhombic Pmmm.
This lost oxygen is entirely re-absorbed during the cooling period, provided that the cooling rate is not too high. Actually, a pure tetragonal phase is obtained at 720°C that irreversibly transforms into the orthorhombic phase up to 800°C. Sintering mechanism is very important, key step for having the superconducting phase. The slight change in the d-spacing of Sample 1 when Y=1.0 and Sample 11 when Gd=1.0 is due to the changes in the ionic radii of Y³⁺(0.940Å) vs Gd³⁺(0.620Å). This complete replacement of Y³⁺ by Gd³⁺ did not significantly effect the lattice parameters and the superconductivity. This supports the belief that Y and Gd layers are not directly involved in the superconductivity mechanism. The presence of two CuO₂ planes with copper in a distorted square planer coordination was suggested as the key for the superconductivity of Y/Gd-Ba-Cu-O system.

It was very interesting to observe that the intensity ratio of the doublet shown in Figure 4-12 around 32.0 to 33.0° was found to vary with the Tc of the samples. Hence, the doublet around 32.0 to 33.0° appears to be directly related to the tetragonal-orthorhombic phase transformation in the case (Y/Gd)-Ba₂Cu₃O₇-δ series which in turn is the main cause of the changes in the Tc values from non-superconducting to the superconducting phase.

4.4: Results of SEM and EDX Studies

(a) Studies of La-(Ba/Sr/Ca)-CuO series

SEM micrographs (Figures 3-24 to 3-26) revealed that all the samples of La-(Sr/Br/Ca)-CuO series having 21-structure system were uniformly mixed, indicating one of the main advantages of the co-
precipitation method. Sample D was more condensed, with small grain size compared to

![Graph showing variation of $T_c$ with intensity ratio $I_1/I_2$.](image)

Figure 4-12: Variation of $T_c$ with the intensity ratio ($I_1/I_2$) of the doublet around 32 to 33° of the Y-Ba-CuO system.

Samples A and E. Variation in atomic radii affect the grain growth, which took place during the sintering mechanism. Microstructures were in direct relation with $T_c$ measurements. Although no definitive conclusion can be drawn our results suggest that as the grain size decreases, the $T_c$ also decreases. The grain size range from 0.5 - 4.85 µm with the smaller grains equiaxed, while the larger are irregular in shape. Sample A show grain size of about 4.85 µm ($T_c = 46$ K), while Sample D show grain size of 0.86 mm ($T_c = 38$ K).

It is clear from SEM micrographs and EDX analyses that only one phase was present in all La-(Sr/Ba/Ca)-CuO samples of 21-structure. Also,
quantitative analyses confirmed the cation ratio of 2:1 for the La:Cu in all samples of the La-(Ba/Sr/Ca)-CuO series.

(b) SEM Micrographs and EDX of (Gd/Y)-Ba-CuO series

Figures 3-27 to 3-38 represent SEM micrographs for eleven samples of the (Y/Gd)-Ba-CuO\(_{7-\delta}\) series having 123-structure. The grain sizes generally range from 2.0-11 \(\mu\text{m}\), where the smaller grains were equiaxed, while the larger were irregular in shape. These differences in grain sizes may be due to the differences in the heating conditions. As more heating was applied to these samples, the grain sizes increase and the samples become more dense which might be due to the formation of orthorhombic phase.

The co-precipitation method gives more reactive powder that react at lower temperature.\(^{40}\) In general, the method developed here produces an homogeneous particle morphology with smooth grain boundaries and smaller spherical particles.

Some authors have suggested that superconducting phase exist on the surface or on grain boundaries of normally conducting material.\(^{57}\) Sintering mechanism was of practical importance because it was the way to control the development of the microstructure.\(^{63}\)

Samples 2, 6 and 10 micrographs (Figures 3-29, 3-33, and 3-37) exhibited a drastic grain growth after annealing for 12 hrs at 900°C in oxygen atmosphere. The fracture, which was often intergranular, presents frequently glassy phase faces. Samples with more yttrium than gadolinium show more fractures. It has been noticed that because of annealing procedures, the shrinkage was lower in yttrium rich compounds.\(^{56}\)
Sample 3 micrographs (Figure 3-30) revealed small grains of 0.11 mm distributed on the grain surface of 7.5 mm in sizes. Sample 4 micrographs Figure (3-31) show the presence of two layers among the sample. At (X4000) magnification these grains show as if they are in layers parallel to each other. In fact the surface affects on the superconducting properties, whether in a mixed phase or in layered phase.(4)

Quantitative analysis (Table 3-6), confirmed the ratio for most samples in 123-structure system being 1Y:2Ba:3Cu respectively. It should be noted that grains were often found that yielded compositions which deviated from \((Y/Gd) - Ba_2Cu_3O_{7-d}\) stoichiometry, because of Cu-deficiency among these grains.

4.5: Resistance versus Temperature Measurements

Nine samples for \(La-(Sr/Ba/Cu)CuO\) series and 11 samples for \((Y/Gd)-Ba-CuO_{7.5}\) series were studied using resistance vs temperature measurements.

(a) \(T_c\) Measurements of \(La-(Sr/Ba/Cu)\)-CuO Series having 21-Structure.

Resistance vs temperature curves for the \(La-(Ba/Sr/Ca)\)-CuO series are shown in Figures 3-42. The resistance was measured over the temperature range 5-298 K. The \(T_c\), \(T_c(\text{onset})\) and transition width for \(La(Br/Sr/Ca)CuO_4\) are listed in Table 4-2. The \(T_c(\text{onset})\) point is defined as the intersection of straight lines extrapolated from the normal-state resistance and the sharp drop in resistance.
All samples exhibited a linear decrease in resistance showing a considerable variations when the concentration of La and Cu was kept constant (equal to that in the Sample A) and Ca and/or Ba were substituted for Sr such that the total alkaline-earth contents in the resulting 4- or 5-component metal oxide systems remained 0.15. The $T_C$ (onset) was reduced by about 17K from $T_C$ of 46K for the Sample A having Sr=0.15 to the $T_C$ of 29K for Sample G having Ca=Ba=0.075, and a 2- to 6-fold broadening was observed in the corresponding transition width (Figure 3-42). However, the $T_C$ remained unchanged for up to 50% substitution of Ba and/or Ca for Sr (Sample E and F). Further substitution of both Ba and Ca for Sr to produce 5-component oxide systems with Sr=Ca=Ba=0.05 (Sample C) resulted in a significant suppression of the $T_C$ as well as $T_C$ (onset) and the transition width increased to 10K (Figure 3-42). Total replacement for Sr by Ca or Ba (Sample D and H), resulted in the reduction of both $T_C$ and $T_C$ (onset). The transition width was 7-10 K for La-Ba-CuO and La-Ca-CuO systems when Ba=Ca=0.15, in contrast to less than 2K in the case of La-(Ba/Sr/Ca)-CuO (Sample A). The $T_C$ for the La-Ba-CuO (Ba=0.15) was about 6 K higher than for the La-Ca-CuO (Ca=0.15) and both were lower than that of the La-Sr-Cu (Sr=0.15) system. An increase in Sr content to 0.4 with concomitant decrease in the La content from 1.85 to 1.60, resulted in suppression of $T_C$ from 36 to 23 K (Figure 3-42).
Table 4-2: Compositional variations and transition temperature data for the La-(Ba/Sr/Ca)-CuO series having 21-structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>$T_c$- (onset)</th>
<th>$T_c$-Transition</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>La$<em>{1.85}$Sr$</em>{0.15}$CuO$_4$</td>
<td>46</td>
<td>35-36</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>La$<em>{1.60}$Sr$</em>{0.4}$CuO$_4$</td>
<td>31</td>
<td>19-24</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>La$_{1.85}$(Sr=Ba=Ca=0.05)CuO$_4$</td>
<td>36</td>
<td>21-31</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>La$<em>{1.85}$Ba$</em>{0.15}$CuO$_4$</td>
<td>38</td>
<td>24-34</td>
<td>10</td>
</tr>
<tr>
<td>E</td>
<td>La$_{1.85}$(Sr=Ba=0.075)CuO$_4$</td>
<td>40</td>
<td>32-36</td>
<td>4</td>
</tr>
<tr>
<td>F</td>
<td>La$_{1.85}$(Sr=Ca=0.075)CuO$_4$</td>
<td>39</td>
<td>26-37</td>
<td>9</td>
</tr>
<tr>
<td>G</td>
<td>La$_{1.85}$(Ca=Ba=0.075)CuO$_4$</td>
<td>29</td>
<td>18-27</td>
<td>9</td>
</tr>
<tr>
<td>H</td>
<td>La$<em>{1.85}$Ca$</em>{0.15}$CuO$_4$</td>
<td>32</td>
<td>20-27</td>
<td>7</td>
</tr>
<tr>
<td>I</td>
<td>La$<em>{1.60}$Ca$</em>{0.40}$CuO$_4$</td>
<td>24</td>
<td>12-22</td>
<td>10</td>
</tr>
</tbody>
</table>

(b) $T_c$ Measurements Of (Y/Gd)Ba$_2$Cu$_3$O$_{7-\delta}$ having 123-Structure

In the case of (Y/Gd)-Ba-CuO series having 123-structure the samples exhibited very minor changes in $T_c$ as a function of compositional variations as shown in Figures 3-43 to 3-53 and Table 4-3. The resistance vs temperature plots for Samples 1-5 and Samples 6-11, respectively are shown in Figure 4-13 and 4-14. The $T_c$ (onset) was reduced by 5.0 K as Y is replaced by Gd in this 123-structure (Sample 1: 96.0 K, Y=1.0, Gd=00; Sample 11: 91 K, Y=0.0, Gd 1.0) and 3 to 6-fold broadening was observed in the corresponding transition width. However, as Gd contents were increasingly substituted in the samples, the $T_c$ (onset) shifted to a lower $T_c$ value. A very large transition width was observed in Sample 2 (Y=0.9 Gd=0.1) and also sample 10 (Y=0.1 Gd=0.9). It was 8 K for both
$Y_{0.6}\text{Gd}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $Y_{0.5}\text{Gd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ systems, where in the case of $Y_{0.4}\text{Gd}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, $Y_{0.3}\text{Gd}_{0.7}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $Y_{0.2}\text{Gd}_{0.8}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ the transition width was 7 K. In contrast to less than 4 K in the case of Gd$_{1.0}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and Y$_{0.7}\text{Gd}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ systems.

Table 4-3: Composition variations and transition temperature data for (Y/Gd)-Ba-CuO series having 123-structure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc (onset)</th>
<th>Tc-Transition</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Y 1.0 Gd 0.0</td>
<td>96.0</td>
<td>87-93</td>
<td>6</td>
</tr>
<tr>
<td>2 Y 0.9 Gd 0.1</td>
<td>95.49</td>
<td>82-95</td>
<td>13</td>
</tr>
<tr>
<td>3 Y 0.8 Gd 0.2</td>
<td>95.10</td>
<td>88-93</td>
<td>5</td>
</tr>
<tr>
<td>4 Y 0.7 Gd 0.3</td>
<td>94.53</td>
<td>92-94</td>
<td>2</td>
</tr>
<tr>
<td>5 Y 0.6 Gd 0.4</td>
<td>94.15</td>
<td>85-93</td>
<td>8</td>
</tr>
<tr>
<td>6 Y 0.5 Gd 0.5</td>
<td>93.52</td>
<td>81-89</td>
<td>8</td>
</tr>
<tr>
<td>7 Y 0.4 Gd 0.6</td>
<td>93.0</td>
<td>88-95</td>
<td>7</td>
</tr>
<tr>
<td>8 Y 0.3 Gd 0.7</td>
<td>92.35</td>
<td>86-93</td>
<td>7</td>
</tr>
<tr>
<td>9 Y 0.2 Gd 0.8</td>
<td>91.90</td>
<td>87-94</td>
<td>7</td>
</tr>
<tr>
<td>10 Y 0.1 Gd 0.9</td>
<td>91.35</td>
<td>80-97</td>
<td>17</td>
</tr>
<tr>
<td>11 Y 0.0 Gd 1.0</td>
<td>91.00</td>
<td>79-82</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 3-46 Resistance vs temperature for the following samples:
1: Y1.0Ba2Cu3O7  2: Y0.9Gd0.1Ba2Cu3O7  3: Y0.8Gd0.2Ba2Cu3O7
4: Y0.7Gd0.3Ba2Cu3O7  5: Y0.6Gd0.4Ba2Cu3O7

Figure 3-47 Resistance vs temperature for the following samples:
6: Y0.5Gd0.5Ba2Cu3O7  7: Y0.4Gd0.6Ba2Cu3O7  8: Y0.3Gd0.7Ba2Cu3O7
9: Y0.2Gd0.8Ba2Cu3O7  10: Y0.1Gd0.9Ba2Cu3O7  11: Gd1.0Ba2Cu3O7
CHAPTER 5
5. CONCLUSIONS

- Both heating and grinding are very important for obtaining the superconducting phase.

- Annealing of the compressed (ca. 30,000 psi) pellets of the black powder of (Y/Gd)-Ba-CuO series for 6-12 hrs under oxygen atmosphere at 900°C was necessary to obtain a superconducting material.

- Oxalate-co-precipitation technique has several advantages over the other procedures:
  (a) smaller grain size
  (b) better homogenity
  (c) ease of conversion of oxalates (than carbonates) to oxides
  (d) reagent grade materials required
  (e) annealing under oxygen atmosphere being not absolutely necessary in the case of La-(Sr/Ba/Ca)CuO series.
  (f) better mixing and stoichiometric ratios
  (g) high reproducibility

- Using oxalate co-precipitation for preparing superconducting material, the following should be carefully observed:

  (a) porcelain crucible is not suitable during firing process,

  (b) intermediate grinding at least twice during the first 12 hours of firing and pelletization is necessary,

- Copper is involved directly in superconductivity while La, Ba and Y are not.
• In the case of 21-structure samples there was no direct relation between peak intensity ratios before and after annealing.

• In the case of 123-structure sample, the intensity ratio of the doublet around 32.0 to 33.0° is found to vary with the $T_C$ of the samples.

• X-ray powder diffraction (XRD) patterns confirmed the presence of a tetragonal phase in all La-(Sr/Ba/Ca)CuO series and the non-superconducting RE-Ba-CuO samples. The presence of an orthorhombic phase was confirmed for all superconducting RE-Ba$_2$Cu$_3$O$_{7-d}$ ceramic systems.

• Scanning Electron Microscopy (SEM) indicated the presence of grain sizes in the range of 0.3 to 15.0 *mm*, while Energy Dispersive X-ray Spectroscopy (EDX) indicated the presence of La:AE ratio of 2:1 for La-(Sr/Ba/Ca)-CuO and 123 for Y:Ba:Cu and the (Y/Gd)-Ba-CuO series.

• The resistance versus temperature measurements indicate Sr being the best alkaline-earth metal among Ca, Ba and Sr for the ternary La-containing ceramics since substitution or doping of Ca and/or Ba for Sr decreased the $T_C$ of these 21- structures.

• The resistance versus temperature data for 123-structures indicated that Y is the best choice among Gd and Y in the RE-Ba$_2$Cu$_3$O$_{7-d}$ series. Substitution or doping of Gd for Y decreased the $T_C$ to a lower value from 96K to about 91K.
- SEM micrographs indicate that samples with more yttrium than gadolinum show more fractures.
CHAPTER 6
6. REFERENCES


(12) (a) W. Meissner and R. Ochsenfeld, Naturwiss, 21, 787 (1933).

(b) H. Frolich, Phys. Rev. 79, 845 (1950).


