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Department of **Metals & Materials Engineering**

The University of British Columbia
Vancouver, Canada

Date **August 14, 1989**
ABSTRACT

The effect of oxygen partial pressure and temperature on the solid state sintering kinetics of the superconducting ceramic \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) has been investigated. The isothermal contraction behavior of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) in the temperature range 930 - 960°C with oxygen partial pressures varying from 0.001 to 1.0 atmospheres was studied. The change in the unit cell lattice parameters of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) over this oxygen partial pressure range was also determined in order to evaluate its effect on the sintering behavior.

The sintering kinetics of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) were investigated through the variation of the isothermal steady state contraction rate with respect to oxygen partial pressure at different temperatures. Isothermal contraction rates between 930 and 955°C reached a maximum at some critical oxygen partial pressure, \( P_0^{\text{CRIT}} \), with decreasing contraction rates both above and below this oxygen partial pressure. This behavior was not observed for \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) sintered at 960°C. SEM micrographs of the fracture surface of these samples suggest that a liquid phase was formed at this temperature. The unit cell volume and a-lattice parameter of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) decreased with decreasing oxygen partial pressure, while the c-lattice parameter increased.

The activation energy for sintering at oxygen partial pressures above \( P_0^{\text{CRIT}} \) has been estimated to be approximately 191 kJ/mole, which is similar to oxygen ion diffusion in this compound, indicating that for oxygen partial pressures above \( P_0^{\text{CRIT}} \), oxygen diffusion is the rate controlling mechanism for mass transport. The activation energy for sintering below \( P_0^{\text{CRIT}} \) was found to be \( \sim 130 \) kJ/mole, which could also be due to oxygen ion diffusion. Several possible factors have been considered for the sintering behavior of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) for oxygen partial pressures below \( P_0^{\text{CRIT}} \). These are formation of copper vacancies, positive hole creation, and lattice strain effect. However, although the oxygen
partial pressure dependence on the sintering rate can be correlated with either the formation of \( \text{Cu}^{2+} \) vacancies in the lattice or hole formation, neither of these mechanisms are considered to be probable.

Mathematically, the contraction rate was found to depend exponentially on the lattice strain \( (\Delta e_{\text{lat}}) \), i.e. \( \dot{\varepsilon} \propto e^{\Delta e_{\text{lat}}} \). The significance of this relationship is not clearly understood. Intuitively, it appears that as the vacancies are created due to the removal of oxygen ions from the lattice, the lattice is not contracting to the extent needed to accommodate the vacancies. This elastic strain hinders the migration of the oxygen vacancies through the lattice, thus affecting the sintering rate of the \( \text{YBa}_2\text{Cu}_3\text{O}_x \) compound below \( P_{O_2}^{\text{CRIT}} \).
# Table of Contents

ABSTRACT .................................................................................................................... ii

Table of Contents ........................................................................................................ iv

List of Figures ............................................................................................................... vi

List of Tables ................................................................................................................ ix

ACKNOWLEDGEMENT ............................................................................................... x

1 INTRODUCTION ....................................................................................................... 1

1.1 Review of the Development of Ceramic Superconductors ........................................ 1

1.1.1 Discovery and Development of Ceramic Superconductors .................................... 1

1.1.2 Potential Applications of Superconductors ............................................................ 5

1.1.3 Phase Equilibria .................................................................................................... 8

1.1.4 Crystal Structure and Oxygen Stoichiometry ......................................................... 12

1.1.5 Powder Production Methods ................................................................................. 20

1.1.5.1 Solid State Synthesis ...................................................................................... 20

1.1.5.2 Coprecipitation .............................................................................................. 21

1.1.5.3 Sol-Gel Synthesis ......................................................................................... 22

1.1.5.4 Other Processes ............................................................................................ 22

1.1.6 Previous Sintering Studies ................................................................................... 23

1.2 Sintering Theories ................................................................................................... 27

1.3 Objectives of Present Study ...................................................................................... 31

2 EXPERIMENTAL PROCEDURE ............................................................................. 32

2.1 Powder Preparation ................................................................................................. 32

2.2 Sample Preparation ................................................................................................. 34

2.3 Experimental Apparatus ......................................................................................... 35

2.3.1 Isothermal Experiments .................................................................................... 35

2.3.1.1 Vertical Tube Furnace ............................................................................... 37

2.3.1.2 Oxygen Probe ............................................................................................ 37

2.3.1.3 Linear Variable Differential Transformer ....................................................... 40

2.3.2 Quenching Experiments ..................................................................................... 42

2.4 Experimental Procedure ......................................................................................... 44

2.4.1 Isothermal Contraction ...................................................................................... 44

2.4.2 Quenching .......................................................................................................... 46

3 RESULTS .................................................................................................................... 47

3.1 Powder Characteristics ......................................................................................... 47
List of Figures

1. Critical temperatures of historic superconductors ........................................ 3
2. Experimental phase diagram of $\frac{1}{2}Y_2O_3$-BaO-CuO .................................. 10
3. Calculated phase diagram of $\frac{1}{2}Y_2O_3$-BaO-CuO ...................................... 10
4. Ternary phase diagram of liquidus surface of $\frac{1}{2}Y_2O_3$-BaO-CuO .................. 10
5. Section through the ternary phase diagram of $\frac{1}{2}Y_2O_3$-BaO-CuO .................. 11
6. Orthorhombic and tetragonal structures of $YBa_2Cu_3O_7$-δ .............................. 13
7. Transition temperature versus oxygen content for $YBa_2Cu_3O_x$ ..................... 14
8. TGA trace for $YBa_2Cu_3O_7$ under 1 atmosphere oxygen ............................... 15
9. TGA traces for $YBa_2Cu_3O_7$ under different oxygen partial pressures ............. 15
10. Lattice parameters of $YBa_2Cu_3O_7$-δ versus temperature ............................. 16
11. Lattice parameters of $YBa_2Cu_3O_7$-δ for various oxygen partial pressures .......... 17
12. Unit cell volume of $YBa_2Cu_3O_7$-δ under various oxygen partial pressures ....... 17
13. Oxygen content of $YBa_2Cu_3O_x$ for temperature and oxygen partial pressure .... 18
14. Isocompositional plot for $YBa_2Cu_3O_7$-δ, log $P_{O_2}$ versus $1/t$ .................. 19
15. Creep strain and relative density versus time ............................................. 24
16. Ratio of densification rate to creep rate .................................................... 25
17. Relation between density, temperature and atmosphere for $YBa_2Cu_3O_7$-δ .... 26
18. Theoretical mass transport mechanisms and paths for neck growth .................. 29
19. Flow diagram of $YBa_2Cu_3O_7$-δ powder production ....................................... 33
20. Experimental equipment used for isothermal contraction experiments ............... 36
21. Cross-section of furnace used in isothermal contraction experiments ................ 39
22. LVDT assembly for isothermal contraction experiments .................................. 41
23. Cross-section of furnace for quenching experiments ..................................... 43
24. Sample arrangement in LVDT assembly ..................................................... 45
25. Particle size distribution of YBa$_2$Cu$_3$O$_{7.8}$ powder ........................................ 48
26. SEM micrographs of YBa$_2$Cu$_3$O$_{7.8}$ powder ....................................................... 48
27. Change in height of sample with time ................................................................. 52
28. Typical contraction plot ..................................................................................... 53
29. Reproducibility plots at two oxygen pressures .................................................. 54
30. Contraction curves at various temperatures in air ............................................. 55
31. Isothermal contraction plots at various oxygen pressures ................................... 56
32. Log contraction - log PO$_2$ plots for various temperatures ................................. 57
33. Log contraction - log PO$_2$ for various oxygen pressures ...................................... 58
34. Log slope - log PO$_2$ for initial contraction slope .................................................. 61
35. Log contraction rate versus log PO$_2$ for 930°C ..................................................... 62
36. Log contraction rate - log PO$_2$ for 945°C ............................................................ 63
37. Log contraction rate - log PO$_2$ for 955°C ............................................................ 64
38. Comparison of log contraction rate - log PO$_2$, at 945 and 960°C ......................... 65
39. Log contraction rate - log PO$_2$ for second batch of powder ............................... 66
40. Arrenhius plots to calculate activation energy ...................................................... 68
41. SEM micrographs of fracture surface at 930°C at various PO$_2$ ......................... 70
42. SEM micrographs of fracture surface at 945°C at various PO$_2$ ......................... 71
43. SEM micrographs of fracture surface at 955°C at various PO$_2$ ......................... 73
44. SEM micrographs of fracture surface at 960°C at various PO$_2$ ......................... 75
45. Typical x-ray diffraction pattern of tetragonal YBa$_2$Cu$_3$O$_{7.8}$ ......................... 78
46. a-lattice parameter versus log PO$_2$ ................................................................. 79
47. c-lattice parameter versus log PO$_2$ ................................................................. 80
48. Unit cell volume versus log PO$_2$ ................................................................. 81
49. Tetragonal structure and oxygen sites for YBa$_2$Cu$_3$O$_{7.8}$ ............................ 87
50. Fractional shrinkage versus $t^{1/3}$ ................................................................. 91
51. Corrected fractional shrinkage versus $t^{1/3}$ .................................................... 92
52. Activation energy plot for sintering of YBa$_2$Cu$_3$O$_{7.8}$ ........................................ 93
53. Thermoelectric power of YBa$_2$Cu$_3$O$_x$ versus oxygen partial pressure .......... 101
54. Thermo electric power of YBa$_2$Cu$_3$O$_x$ versus oxygen content ...................... 101
55. Unit cell volume versus oxygen content ............................................................ 104
56. Unit cell volume as a function of log $P_{O_2}$ ...................................................... 105
57. Lattice strain versus log $P_{O_2}$ ............................................................................. 106
58. Ln contraction rate versus lattice strain .............................................................. 107

I-1. Contraction plots at various $P_{O_2}$ at 930°C ...................................................... 119
I-2. Contraction plots at various $P_{O_2}$ at 930°C ...................................................... 120
I-3. Contraction plots at various $P_{O_2}$ at 945°C ...................................................... 122
I-4. Contraction plots at various $P_{O_2}$ at 945°C ...................................................... 123
I-5. Contraction plots at various $P_{O_2}$ at 955°C ...................................................... 125
I-6. Contraction plots at various $P_{O_2}$ at 955°C ...................................................... 126
I-7. Contraction plots at various $P_{O_2}$ at 960°C ...................................................... 128
List of Tables

1. Critical Temperatures of the RBa$_2$Cu$_3$O$_7$ Family of Compounds .......................... 2
2. Compounds and Critical Temperatures in the (AO)$_m$M$_2$Ca$_{m-1}$Cu$_n$O$_{2n+2}$ Family .... 4
3. Temperatures of Observed Invariant Points in Ternary Diagram ................................. 11
4. Dimensions and Properties of Compacts ........................................................................ 34

I-1. Contraction Rates versus PO$_2$, 930°C ..................................................................... 118
I-2. Contraction Rates versus PO$_2$, 945°C ..................................................................... 121
I-3. Contraction Rates versus PO$_2$, 955°C ..................................................................... 124
I-4. Contraction Rates versus PO$_2$, 960°C ..................................................................... 127
II-1. Characteristic X-ray Diffraction Data for YBa$_2$Cu$_3$O$_{7.5}$ ....................................... 129
III-1. Lattice Parameter versus Oxygen Partial Pressure Data ............................................. 130
ACKNOWLEDGEMENT

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1 INTRODUCTION

1.1 Review of the Development of Ceramic Superconductors

1.1.1 Discovery and Development of Ceramic Superconductors

Prior to 1986, superconductivity was a phenomenon restricted to metals, occurring only at very low temperatures and requiring liquid helium as the refrigerant. The highest known critical transition temperature ($T_c$) was 23 K for the intermetallic compound Nb$_3$Ge. In the early part of 1986 Bednorz and Muller,\(^1\) two IBM researchers in Switzerland, discovered that a mixed oxide of lanthanum, barium and copper became superconducting at a temperature of 30 K.

This generated a great deal of interest in the scientific community for a number of reasons. The first is the unexpected occurrence of superconductivity at such relatively high temperatures. The prevailing view prior to 1986 was that the maximum $T_c$ obtainable was close to that of Nb$_3$Ge. Moreover, the fact that the material was an oxide was very surprising, due to its' low concentration of charge carriers.

Several months later it was discovered\(^2\) that by substituting strontium for barium, producing the compound corresponding to La$_{1.8}$Sr$_{0.2}$CuO$_4$, a critical temperature above 35 K could be obtained. The intense research effort unleashed by these announcements has led to an explosion in the number of oxide superconductors, with higher and higher transition temperatures.

In February of 1987 Wu and Chu\(^3\) announced the discovery of YBa$_2$Cu$_3$O$_7$, or '123' as it is now known, with a transition temperature of 90 K. This was of great technological importance, as superconductivity at liquid nitrogen temperatures (77 K) was at last achieved. Subsequent research has led to the development of two other notable oxide
superconductors; Bi$_2$Sr$_2$CaCu$_2$O$_8$ with a transition temperature of 110 K, and Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ with a transition temperature of 122 K. This last superconductor has the highest confirmed value of $T_c$ to date. Figure 1 shows the critical temperatures of historic superconductors against their discovery date. This illustrates the dramatic increase in $T_c$ achieved by the oxide superconductors.

One of the interesting features of these ceramic superconductors is the ability to make chemical substitutions for certain elements without seriously degrading their superconducting properties. Table 1 shows the critical temperatures of the RBa$_2$Cu$_3$O$_{7.8}$ family, where R is given. The other large class of ceramic superconductors is of the type (AO)$_m$M$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2}$, where the A cation can be thallium, bismuth, lead or a mixture of these elements, the value of m is 1 or 2, and the M cation is barium or strontium. The number of consecutively stacked CuO$_2$ layers is indicated by n. The superconducting compounds in this family and their transition temperatures are listed in Table 2.

<table>
<thead>
<tr>
<th>R</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>91</td>
</tr>
<tr>
<td>Nd</td>
<td>92</td>
</tr>
<tr>
<td>Sm</td>
<td>88</td>
</tr>
<tr>
<td>Eu</td>
<td>94</td>
</tr>
<tr>
<td>Gd</td>
<td>92</td>
</tr>
<tr>
<td>Dy</td>
<td>91</td>
</tr>
<tr>
<td>Ho</td>
<td>91</td>
</tr>
<tr>
<td>Er</td>
<td>91</td>
</tr>
<tr>
<td>Tm</td>
<td>91</td>
</tr>
<tr>
<td>Yb</td>
<td>86</td>
</tr>
<tr>
<td>Lu</td>
<td>88</td>
</tr>
</tbody>
</table>
Figure 1. Critical temperatures of superconductors, with their discovery date, and the key operating temperatures of liquid helium, hydrogen and nitrogen.
Table 2. Compounds and Critical Temperatures in the \((\text{AO})_n\text{M}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}\) Family

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_c) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{TlBa}_2\text{CaCu}_2\text{O}_7)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9)</td>
<td>110</td>
</tr>
<tr>
<td>(\text{TlBa}_2\text{Ca}_3\text{Cu}<em>4\text{O}</em>{11})</td>
<td>122</td>
</tr>
<tr>
<td>(\text{Tl}<em>{1}\text{Bi}</em>{2}\text{Sr}_2\text{Cu}_2\text{O}_5)</td>
<td>50</td>
</tr>
<tr>
<td>(\text{Tl}<em>{1}\text{Bi}</em>{2}\text{Sr}_2\text{CaCu}_2\text{O}_7)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{Tl}<em>{1}\text{Pb}</em>{2}\text{Sr}_2\text{Cu}_2\text{O}_7)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{Tl}<em>{1}\text{Pb}</em>{2}\text{Sr}<em>{1}\text{Ca}</em>{2}\text{Cu}_3\text{O}_9)</td>
<td>122</td>
</tr>
<tr>
<td>(\text{Tl}_{3}\text{Ba}_2\text{Cu}_2\text{O}_6)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{Tl}_{3}\text{Ba}<em>2\text{Ca}</em>{1}\text{Cu}_2\text{O}_8)</td>
<td>110</td>
</tr>
<tr>
<td>(\text{Tl}_{3}\text{Ba}_2\text{Ca}_2\text{Cu}<em>2\text{O}</em>{10})</td>
<td>122</td>
</tr>
<tr>
<td>(\text{Tl}_{3}\text{Ba}_2\text{Ca}_3\text{Cu}<em>4\text{O}</em>{10})</td>
<td>119</td>
</tr>
<tr>
<td>(\text{Bi}_{3}\text{Sr}_2\text{Cu}_2\text{O}_6)</td>
<td>12</td>
</tr>
<tr>
<td>(\text{Bi}_{3}\text{Sr}<em>2\text{Ca}</em>{2}\text{Cu}_2\text{O}_8)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{Bi}_{3}\text{Sr}<em>2\text{Ca}</em>{2}\text{Cu}<em>3\text{O}</em>{10})</td>
<td>110</td>
</tr>
<tr>
<td>(\text{Bi}_{3}\text{Sr}_2\text{Ca}_3\text{Cu}<em>4\text{O}</em>{12})</td>
<td>90</td>
</tr>
</tbody>
</table>

For the purposes of this study, only the \(\text{YBa}_2\text{Cu}_3\text{O}_{7.8}\) superconductor was considered. There are several reasons for this. At the start of this study, the \((\text{AO})_n\text{M}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}\) family of superconductors had not yet been discovered. The \(\text{YBa}_2\text{Cu}_3\text{O}_{7.8}\) system is relatively simple to produce and handle. Finally, the \(\text{YBa}_2\text{Cu}_3\text{O}_{7.8}\) system has only one superconducting phase which has been extensively investigated. There have been an estimated 3000 articles written on \(\text{YBa}_2\text{Cu}_3\text{O}_{7.8}\) between May 1 and November 15, 1987. On average this translates into a rate of 15 articles per day. These have started 11 newsletters to report what is happening in superconductivity and new sections added to six existing newsletters. Furthermore, in a two month span (June-July 1987), there were 70 different meetings on high temperature superconductivity.

This flurry of activity includes determining the structure of \(\text{YBa}_2\text{Cu}_3\text{O}_{7.8}\) by x-ray and neutron diffraction and muon-spin relaxation measurements; the development of ternary phase diagrams and phase relationships; powder production methods;
superconducting parameters and properties; oxygen diffusion and mechanical properties; fabrication techniques for producing a variety of components from wire to bulk samples; and development of a possible theory of superconductivity. These experimental efforts have, however, neglected to investigate some of the fundamental aspects of component production from a ceramics viewpoint. The densification mechanisms and kinetics and sintering procedures, effects of grain size and impurities on microstructure development and their resulting mechanical and superconducting properties that are necessary for the production of useful superconducting components have received little attention.

1.1.2 Potential Applications of Superconductors

As this is the first thesis on ceramic superconductors presented in this department, a brief outline of the impact of the discovery of ceramic superconductors is considered to be desirable. It is for this reason that this section is included.

When the discovery of high-temperature ceramic superconductors was first announced, it was likened to such technological milestones as the invention of the lightbulb and the transistor. Newspaper articles predicted that magnetically levitated trains and desktop supercomputers would be on the marketplace in a matter of months. This enthusiasm has since been tempered somewhat by the realization that many obstacles must be overcome before the new materials can become commercial reality. These obstacles include fabricability, current carrying capacity and long-term environmental stability.

The economic prospects for ceramic superconductors are, however, very bright. There is an already viable marketplace created by conventional superconductors as well as unique applications not feasible for metallic superconductors. Conventional superconductors have built a $300 million global market serving a number of industries.
Raising operating temperatures for superconductors from the current 4.2 K to 77 K can expand these markets because of the lower cost and greater simplicity of liquid nitrogen cooling methods.

In one hour one watt of heat will evaporate 1.4 litres of liquid helium or 0.016 litres of liquid nitrogen. To replace this loss would cost $50,000 a year for liquid helium (at $4 per litre), compared with $35 for liquid nitrogen (at 25 cents per litre). For large scale operations in which refrigeration is a minor part of the total cost, switching to liquid nitrogen would not have much of an economic benefit. The switch to liquid nitrogen would have a much bigger impact on small scale applications, which are expensive to cool with liquid helium because of their large surface to volume ratio. Also, with the reduction in thermal insulation, devices can be made more compact and portable. Therefore, it is felt that ceramic superconductors will first be introduced in small scale applications.

The current superconducting industry can be broken down into three major categories: superconducting magnets, electronics and large scale applications (e.g. electric power, transportation).

Magnets are essential to every electrical generator and motor. Lighter, more powerful magnets are possible with superconductors, producing higher power to weight ratios for motors and more compact generators with higher efficiencies.

Magnetic separators are used to separate iron and steel products and to remove impurities from food and raw materials such as alumina, clay and sand. Superconducting separators consume 95% less electricity than a conventional system.

One of the latest medical diagnostic tools, magnetic-resonance imaging, uses a superconducting magnet to align hydrogen nuclei in the body. This can be used to produce 'x-ray' images of the soft tissue in the body. Superconducting magnets can also
be used in conjunction with paramagnetic and ferromagnetic materials to achieve extraordinarily low temperatures. In the laboratory, magnetic refrigerators have achieved temperatures as low as $10^{-6}$ K. A SQUID can measure voltage differences as small as $10^{-18}$ volts, currents as small as $10^{-18}$ amperes and magnetic fields of less than $10^{-14}$ tesla. No other technology can come close to these values.

Physicists employ SQUIDs to search for quarks, monopoles and gravitons. Geologists prospect for oil, water and mineral deposits, which cause local anomalies in the earth's magnetic field. SQUIDs are also used to search for submarines and sunken ships. In the future, SQUIDs may detect tiny ion currents in corroding metals.

SQUIDs are also used to detect the faint magnetic signals associated with electrical activity in the heart and brain, in a technique called magnetoencephalography. This technique can detect the source of a nerve signal to within a few millimeters.

Applications for ceramic superconductors in large scale operations are limited. In the generation of electricity, conventional generators are very efficient and little benefit would be gained. One potential application is in the storage of electricity in a superconducting magnetic energy storage (SMES) system. A SMES system would allow a utility to store excess energy during times of overproduction (at night), with no energy loss, and then tap it when demand exceeds generating capacity (during the day). Other
applications include transmission lines and surge protectors.

One of the more widely discussed application of superconductors is the magnetically levitated train. High temperature superconductors would improve engineering reliability but would not reduce costs much, as the refrigeration cost is miniscule compared to the total capital investment and operating costs.

A more detailed review of the present and potential applications for high temperature superconductors, as well the current and projected economics of these applications, are given in references 4 to 9.

1.1.3 Phase Equilibria

An accurate knowledge of the phase relationships in the Y$_2$O$_3$-BaO-CuO system at high temperature, including liquid formation, is important to optimize the thermal processing of YBa$_2$Cu$_3$O$_{7-8}$. Such thermal processing includes calcination of raw materials, fabrication of superconducting components and articles by sintering, melt spinning or plasma spraying, and growth of single crystals.

Many researchers have attempted to find the subsolidus relationships in the Y$_2$O$_3$-BaO-CuO system, and their results do not necessarily agree. This is due to the extremely complicated nature of the system. It has all the classical complexities of a ternary oxide system, plus several of its own. Temperature, oxygen partial pressure and cooling rates all have a marked effect on the structure. In addition, the hydration of the barium-rich binary compounds, the reactivity of the reagents with crucible materials and the environmental instability of the superconducting compound can introduce difficulties in determining the correct phase relationships. These difficulties have limited most investigations to subsolidus, isothermal phase relationships.
Research investigating the liquidus fields in the ternary system has been limited.\textsuperscript{10,14} Lee and Lee\textsuperscript{16} used thermodynamic data to calculate equilibrium liquidus surfaces and isothermal surfaces at several temperatures in the Y\textsubscript{2}O\textsubscript{3}-BaO-CuO ternary system. However, they noted that "all of the phase diagrams in this paper should be further refined when measured data are available." One further complication involved in liquidus field investigation is the effect of processing of the raw materials on the formation of liquid phases. It has been found\textsuperscript{12} that low temperature liquid formation can occur due to chemical inhomogeneity in the powder.

Figure 2 shows the experimental phase diagram of Y\textsubscript{2}O\textsubscript{3}-BaO-CuO at 950 - 1010°C in air. This figure also shows the best effort at depicting the primary phase field of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta}. Figure 3 shows the calculated phase diagram of 1/2(Y\textsubscript{2}O\textsubscript{3})-BaO-CuO in air, showing the liquidus surface. A detailed study\textsuperscript{10} of the liquidus surface in the copper-rich portion of the ternary diagram has resulted in Figure 4. The temperatures of the invariant points and explanation of the labels used for the primary phase fields are given in Table 3. Figure 5 shows a section through the 123-211 join.

There are several features of these phase diagrams that should be noted. The first is that YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} has an incongruent melting point of 1015°C. This is a fairly low temperature that is well within reach of industrial furnaces. However, 123 products cannot be produced through a melt and cast process as 123 dissociates upon melting, forming non-superconducting phases.

A second feature to be noted is that 123 is stable with a liquid phase above ~960°C. This liquid is copper-rich with respect to 123. Therefore, if the stoichiometry is slightly off, or if complete homogenization has not been achieved, a liquid phase will be produced above 960°C.
Figure 2. Experimental phase diagram of $1/2Y_2O_3$-BaO-CuO system.[11]

Figure 3. Calculated phase diagram of $1/2Y_2O_3$-BaO-CuO system (liquidus surface).[16]

Figure 4. Ternary phase diagram of the liquidus surface in the system $1/2Y_2O_3$-BaO-CuO in equilibrium with air. The positions of all boundary curves and invariant points are approximate.[10]
Table 3. Temperature of observed invariant points and primary crystallization field labels for use with figures 4 and 5.[10]

<table>
<thead>
<tr>
<th>Invariant Point*</th>
<th>Temperature (°C)</th>
<th>Field label</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>e1</td>
<td>890</td>
<td>200</td>
<td>Y₂O₃</td>
</tr>
<tr>
<td>e2</td>
<td>920</td>
<td>001</td>
<td>CuO</td>
</tr>
<tr>
<td>p1</td>
<td>940</td>
<td>202</td>
<td>Y₂Cu₂O₅</td>
</tr>
<tr>
<td>p2</td>
<td>975</td>
<td>011</td>
<td>BaCuO₂</td>
</tr>
<tr>
<td>c3</td>
<td>1000</td>
<td>211</td>
<td>Y₂BaCuO₅</td>
</tr>
<tr>
<td>p3</td>
<td>1000</td>
<td>210</td>
<td>Y₂BaO₄</td>
</tr>
<tr>
<td>m1</td>
<td>1015</td>
<td>123</td>
<td>YBa₂Cu₃O₆</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>m4</td>
<td>1270</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The letter "e" is used for eutectics, "p" for peritectics and "m" for melting points.

Figure 5. Section through the ternary phase diagram along the join YBa₂Cu₃O₆-Y₂BaCuO₅. Positions of all lines are approximate, except for the incongruent melting point of YBa₂Cu₃O₆.[10]
1.1.4 Crystal Structure and Oxygen Stoichiometry

The common structural feature of all the new high $T_c$ ceramic superconductors is the presence of one or more CuO$_2$ planes. In some structures these planes occur in groups, which are separated by one layer (typically yttrium or calcium) and intercalated by a variable number of other layers (eg. BaO, CuO, BiO, etc.).$^{17}$

The YBa$_2$Cu$_3$O$_{7-8}$ structure has been extensively studied by different groups using x-ray powder diffraction$^{19-24}$ and neutron powder diffraction$^{24-27}$ measurements. These investigations have determined that the structure of the superconducting YBa$_2$Cu$_3$O$_7$ phase is orthorhombic (space group Pmmm) with lattice parameters, $a=3.829$ Å, $b=3.888$ Å and $c=11.678$ Å at room temperature.$^{24}$ The unit cell consists of three distorted perovskite building blocks, which contain copper atoms at the corners, oxygen atoms on the cube edges between the copper atoms and ordered metal ions (yttrium or barium) in the center of the cube. The yttrium plane is totally devoid of oxygen, the Cu-O planes adjacent to the yttrium plane are two-dimensional ("CuO$_2$ planes"), whereas the Cu-O plane located between the Ba-O planes exhibits ordered oxygen vacancies. This results in one dimensional CuO chains along the b-axis. This structure is shown in Figure 6a.

These investigations also revealed that there is a structural phase transition between the superconducting orthorhombic phase (YBa$_2$Cu$_3$O$_7$) and a non-superconducting tetragonal phase (YBa$_2$Cu$_3$O$_6$). The tetragonal structure has space group P4/mmm$^{26}$ with lattice parameters $a=b=3.852$ Å and $c=11.73$ Å at room temperature.$^{65}$ The tetragonal structure is similar to the orthorhombic structure, except that the oxygen atoms occupying the b-axis have been removed. This structure is shown in Figure 6b. The orthorhombic-tetragonal phase transition is an order-disorder reaction, and occurs when the oxygen stoichiometry in YBa$_2$Cu$_3$O$_x$ is approximately equal to $x=6.6$. $^{20}$
The control of oxygen content in a YBa$_2$Cu$_3$O$_x$ sample is very important. As the oxygen content, $x$, decreases from a maximum of 7, $T_c$ decreases as well. This is shown in Figure 7. Both orthorhombic and tetragonal phases show a monotonic decrease in oxygen content with temperature. This has allowed the use of thermogravimetric analysis (TGA) to determine the oxygen content of YBa$_2$Cu$_3$O$_{7.8}$ samples.\textsuperscript{18-21,28,29} It has been shown\textsuperscript{19} that the weight loss experienced by YBa$_2$Cu$_3$O$_{7.8}$ upon heating is due solely to changes in oxygen stoichiometry. The oxygen stoichiometry in a sample is determined by the oxygen partial pressure and cooling rate experienced by the sample.
A TGA trace for YBa$_2$Cu$_3$O$_y$ heated and cooled under 1 atmosphere of oxygen is shown in Figure 8. It can be seen that oxygen stoichiometry is completely reversible. TGA traces for YBa$_2$Cu$_3$O$_{7.8}$ heated and cooled under various oxygen partial pressures are shown in Figure 9. In Figure 9a an orthorhombic sample is heated and cooled in argon, showing an irreversible loss of oxygen. However, when the resulting sample is heated and cooled in oxygen the initial oxygen stoichiometry is regained. Figure 9b illustrates the importance of cooling rate on the oxygen stoichiometry of the resulting material. A tetragonal sample is heated in air and then quenched, resulting in a slight increase in oxygen stoichiometry. The full increase in oxygen stoichiometry is only obtained after slow cooling in air.
Figure 8. TGA trace for YBa$_2$Cu$_3$O$_{7-\delta}$ heated and cooled under 1 atmosphere oxygen, showing completely reversible stoichiometry.

Figure 9. TGA traces for YBa$_2$Cu$_3$O$_{7-\delta}$ heated and cooled in different partial pressures of oxygen. Each treatment sequence can be visualized by starting at the star and following the arrows. a) The as-prepared sample is heated under argon, cooled in argon and reheated in oxygen. b) A vacuum annealed sample is heated in air, quenched in air, reheated in air and slow cooled in air.[18]
As the superconductor is heated the lattice parameters change, due to thermal expansion and changes in oxygen stoichiometry. This can be seen in Figure 10. With 1 atmosphere of oxygen the orthorhombic-tetragonal transition occurs at approximately 700°C.

The effects of oxygen partial pressure on the orthorhombic-tetragonal transition temperature is shown in Figure 11. It can be seen that the orthorhombic-tetragonal transition temperature decreases with decreasing oxygen pressure. A trend towards larger lattice constants, particularly in the c-direction, is observed as the oxygen pressure is reduced. This is also reflected in the increasing unit cell volume with decreasing oxygen partial pressure, Figure 12.

Figure 10. Lattice parameters versus temperature for YBa$_2$Cu$_3$O$_x$ in 1 atmosphere oxygen.[26]
Figure 11. Lattice parameters versus temperature for YBa$_2$Cu$_3$O$_x$ under various oxygen atmospheres. Lines are guides to the eye. [20]

Figure 12. Unit cell volume as a function of temperature for YBa$_2$Cu$_3$O$_{y.8}$ under various oxygen atmospheres. Lines are guides to the eye. [20]
As stated previously, the oxygen content in a YBa$_2$Cu$_3$O$_x$ sample can be determined by TGA for various temperatures and oxygen partial pressures, Figure 13. From this data an empirical equation for the value of $x$ at a given temperature and oxygen partial pressure was obtained by Gallagher:

$$x = (5.39 \pm 0.02)P O_2^{0.0075 \pm 0.0004} \exp \left( \frac{199 \pm 5}{T} \right)$$

(1)

Figure 13. Oxygen content from TGA analysis at various temperatures and oxygen atmospheres. Open squares show reproducibility measurements made at the highest and lowest pressures.[20]
Single phase YBa$_2$Cu$_3$O$_x$ has 2 degrees of freedom at atmospheric pressure, as the cationic composition is fixed at Y/Ba/Cu = 1/2/3 by compositional necessity for high T$_c$ superconductivity.$^{31}$ As the two independent thermodynamic variables, one may choose temperature, T, and oxygen partial pressure, PO$_2$, or its conjugate extensive parameter x via an equation of state with respect to the oxygen content, $x=x(T,PO_2)$. This says that the composition of YBa$_2$Cu$_3$O$_x$ is fixed if temperature and PO$_2$ are known.

By combining oxygen content versus temperature and PO$_2$ pressures with structural data, isocompositional plots of YBa$_2$Cu$_3$O$_x$ can be constructed, Figure 14. This figure also indicates the regions of stability of tetragonal and orthorhombic YBa$_2$Cu$_3$O$_{7.5}$.

Figure 14. Isocompositional plot of YBa$_2$Cu$_3$O$_{7.5}$, log PO$_2$ versus reciprocal temperature. The dashed line represents the conditions for the orthorhombic to tetragonal transformation.[33]
1.1.5 Powder Production Methods

A variety of processing techniques based on current technologies for producing advanced ceramics have been adapted to producing YBa$_2$Cu$_3$O$_{7.8}$. These include solid state synthesis, coprecipitation, sol-gel synthesis, freeze-drying and colloidal methods.

The value of the transition temperature is only marginally affected by the route of powder processing. Transition temperatures are primarily affected by the sintering conditions (temperature, cooling rate and atmosphere) experienced by the powder. The main reason for looking at different powder processing routes is to optimize the critical current density in polycrystalline materials. This may be accomplished by the use of needle shaped grains aligned in the current carrying direction, reduction in porosity and the reduction of impurities and nonsuperconducting materials at the grain boundaries.$^{34}$

A short review of several of the processes as it pertains to the production of YBa$_2$Cu$_3$O$_{7.8}$ is given below.

1.1.5.1 Solid State Synthesis

This is the most common method of producing YBa$_2$Cu$_3$O$_{7.8}$ powder. Appropriate quantities of Y$_2$O$_3$, BaO$_2$ and CuO are thoroughly mixed and calcined. The calcination temperature should be as high as possible to promote complete reaction and achieve homogenization. The temperature should be kept below 960°C, however, to avoid liquid phase formation during reaction, as discussed in a previous section. It has been found$^{62}$ that a calcination temperature of 950°C produces powder with optimum superconducting properties.

Other possible sources of barium used in solid state synthesis include BaO and BaCO$_3$. Both compounds, however, present problems during synthesis. The
decomposition of BaCO₃ appears to be the rate limiting step during calcination of these powders. Any undecomposed BaCO₃ present in the powder during sintering can produce CO₂, thus creating a gas phase barrier which would prevent oxygen diffusion and possibly densification. In addition, carbon can be retained in the powder, degrading superconducting properties.

Barium oxide would appear to be an ideal source of barium. However, it is very hygroscopic and therefore presents problems in the weighing of the powder to obtain stoichiometry needed for YBa₂Cu₃O₇.8.

To ensure a homogeneous product, the powder must be calcined more than once, with intermediate grindings. The grinding has been accomplished by mortar and pestle, ball milling and attrition milling. The milling can be done in either acetone, isopropyl alcohol, or ethanol. However, it has been suggested that even 5 grind/calcination steps will not completely homogenize the powder. This inhomogeneity is the major drawback of powders produced by this method.

1.1.5.2 Coprecipitation

The coprecipitation method produces finely divided powders with better homogeneity and lower impurity levels than solid state synthesis. There are a variety of processes available to coprecipitate YBa₂Cu₃O₇.8.

One such process dissolves BaCO₃ and Y₂O₃ in hot dilute nitric acid. Cupric nitrate is then added before the solution is cooled to room temperature. Oxalic acid is added and the pH is adjusted by the addition of ammonium hydroxide. The resulting slurry is then filtered, washed and dried. The dried slurry is ground and calcined to produce YBa₂Cu₃O₇.8 powder. The resulting grain size distribution is narrow with an
average size of \( \sim 0.3 \) microns.

Variations on this procedure are dissolving the reactants in methyl alcohol and oxalic acid\(^\text{42}\) or in concentrated nitric acid\(^\text{43}\) and evaporating the supernatant fluid. Nitrate solutions have also been produced by dissolving copper metal\(^\text{44}\) and precipitating with oxalic acid.

There are a few drawbacks to this process. Careful control of pH is required to produce fine particle sized, homogeneous powders.\(^\text{45,46}\) Also, coprecipitated powders may have small impurity levels of the precipitating agents which are difficult to remove by washing.

1.1.5.3 Sol-Gel Synthesis

Preparation of a sol-gel involves the dissolution of copper metal in nitric acid, to which \( \text{Y(NO}_3\text{)}_3 \) and \( \text{BaCO}_3 \) are added.\(^\text{43}\) After the pH is adjusted to 7, polyacrylic acid is added. Immediate chelation of the cations occurs, gelling the material. The gel is dried and calcined to give \( \text{YBa}_2\text{Cu}_3\text{O}_{7.5} \). This process produces fine, homogeneous powders, but is time consuming and requires expensive raw materials.

1.1.5.4 Other Processes

Other methods have been developed to produce powders, including colloidal processing,\(^\text{35,47}\) freeze-drying\(^\text{48}\) and alkoxide processing.\(^\text{35}\) All of these processes have shown initial promise in producing fine powders, but more work must be done to fully characterize these processes.
1.1.6 Previous Sintering Studies

A variety of techniques have been used to fabricate components of YBa$_2$Cu$_3$O$_{7.8}$. These include traditional ceramic processing techniques such as pressureless sintering, hot pressing, tape casting and extrusion. More novel techniques include sinter-forging and dynamic compaction. However, many of these fabricating techniques degrade or destroy superconducting properties, and require elaborate annealing procedures to restore these properties. Therefore, pressureless sintering is one of the most viable techniques for producing bulk samples with optimum superconducting properties.

Several pressureless sintering studies have been carried out on YBa$_2$Cu$_3$O$_{7.8}$. These have included the densification properties, effects of sintering atmosphere and liquid phases on density and microstructural development.

Rahaman et al. sintered compacts in air between 910 and 940°C. They applied small, constant uniaxial stresses to the compacts during sintering. The applied stresses caused extensive creep, but only a small increase in density, in comparison to pressureless sintering, as shown in Figure 15. The ratio of densification rate ($\dot{\varepsilon}_p$) to creep rate ($\dot{\varepsilon}_c$) during the intermediate stage of sintering is plotted in Figure 16 together with those for CdO and ZnO (solid state sintering), a soda-lime glass (viscous flow), and MgO-5 wt% Bi$_2$O$_3$ (liquid phase). It can be seen that $\dot{\varepsilon}_p/\dot{\varepsilon}_c$ for YBa$_2$Cu$_3$O$_{7.8}$ falls between the data for solid state sintering and glass, but is close to that for the MgO-Bi$_2$O$_3$ system. From this data it was concluded that a liquid phase was present during sintering. However, the YBa$_2$Cu$_3$O$_{7.8}$ powder used was produced with BaCO$_3$ and calcined at 850°C, which would not provide adequate homogenization and can lead to low temperature liquid formation.
Figure 15. a) Creep strain versus time for 0, 70 and 140 kPa.  b) Relative density versus time for 0 and 140 kPa.[58]
Figure 16. Ratio of densification rate to creep rate versus relative density for YBa$_2$Cu$_3$O$_{7.5}$ compared with data for other ceramic powders. Data has been normalized at a constant uniaxial stress of 200 kPa.[58]

Studies of solid state sintering with respect to atmosphere have indicated that there is a relationship between sintered density and sintering atmosphere.$^{59,63-65}$ Tsuda et al.$^{64}$ found that decreasing partial pressures of oxygen resulted in lower temperatures needed to obtain a desired density, Figure 17. It was noted in this study that specimens which were sintered above the peak density temperature for each atmosphere resulted in a multiphase mixture with lower densities.
Rha et al.\textsuperscript{63} sintered compacts at 850°C for 12 hours in either helium or oxygen. The porosity of the specimen sintered in helium was 26% compared to 38% for that sintered in oxygen. The grain size of the specimen sintered in helium was 1.3 times larger than that sintered in oxygen. This indicates a faster atom diffusion rate in an inert environment than in oxygen. It was postulated that this is due to either a higher oxygen vacancy concentration or to an expanded unit cell.

Liquid phases, produced by changes in stoichiometry or sintering close to the melting point, enhance densification and increase grain growth.\textsuperscript{66-68} Huang et al.\textsuperscript{67} adjusted the stoichiometry of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} to Y/Ba/Cu=0.8/2/3 to obtain a liquid phase during sintering at 950°C in oxygen. A porosity of 9% was obtained, while 26% porosity was obtained for YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} sintered by the same procedure. However, critical current densities were degraded from 33 A/cm\textsuperscript{2} for the specimen with 26% porosity to 0 A/cm\textsuperscript{2} for the specimen with 9% porosity. The liquid phases produced are non-superconducting and wet the grain boundaries of the superconducting grains. TEM analysis\textsuperscript{69} has shown that liquid phases are concentrated around pores and extend back along grain boundaries.
adjacent to these pores. This reduces the effective contact area between the superconducting grains and degrades superconducting properties. Therefore liquid formation during sintering should be avoided.

1.2 Sintering Theories

When a powder compact is heated to temperatures above one half of the homologous temperature \( T_m \) (where \( T_m \) is the melting point in Kelvin), the powder particles initially weld together and as the weld zone subsequently increases, the density of the compact changes. This process is known as sintering. This can occur purely in the solid state, in the presence of a liquid or under an applied stress.

The process of sintering, complex by itself, is further complicated by other concurrent processes which occur at elevated temperatures, such as grain growth, particle rearrangement, phase transformations and chemical reactions. Many attempts have been made to develop an understanding of the phenomena occurring during sintering, with varying degrees of success. Investigation of the sintering phenomena occurring between two individual particles has been fairly successful. Extending these findings to predict the full sintering behavior of a compact of a large number of particles has not, however, been very successful.

Several techniques have been used to study sintering kinetics. These include looking at the development of necks between spherical particles, spheres on plates and between wires, shrinkage measurements of powder compacts, and changes in electrical resistivity and porosity with sintering time and temperature. Most researchers, however, have used either neck growth measurements or shrinkage experiments to study sintering kinetics.
In order for sintering of a powder compact to proceed, mass transport of material to the contact points between the particles must occur. This mass transport can occur by a number of different mechanisms. Kuczynski\textsuperscript{71} was the first to derive equations for neck growth between two particles in contact based on these mass transport mechanisms, and experimentally verified his theoretical work. He found that the ratio of neck radius ($y$) to particle radius ($a$) was a function of time. Subsequent studies by a number of researchers\textsuperscript{72-74} has resulted in the same generalized equation:

$$\left( \frac{y}{a} \right)^n = \frac{FD\gamma\Omega t}{a^m kT}$$

(2)

where $\gamma$ is the surface tension, $\Omega$ is the molar volume, $D$ is the diffusion coefficient, $k$ is Boltzmann's constant, $T$ is temperature (Kelvin) and $t$ is time. The constants $n$, $m$ and $F$ vary according to the neck growth mechanism and diffusion path that is operating.

There are a variety of theoretical mass transport mechanisms that can operate during sintering. This includes viscous flow, evaporation-condensation and diffusion. The diffusion mechanisms can be further classified according to the path of diffusion, and the source of material being transported to the neck. Diffusion can occur through surface, volume or grain boundary paths from surface, volume or grain boundary sources. These various mass transport mechanisms and paths are shown in Figure 18.

From the neck growth equations of Kuczynski\textsuperscript{71}, equations for the shrinkage of compacts of spherical particles were developed. These theoretical equations relate the normalized linear shrinkage $\left( \frac{\Delta L}{L_0} \right)$ to time ($t$). Both Kingery and Berg\textsuperscript{73} and Coble\textsuperscript{74} obtained the following linear shrinkage equation for a compact of spherical powders:

$$\left( \frac{\Delta L}{L_0} \right) = \left( \frac{10D\gamma\Omega}{a^3 kT} \right)^{0.4} t^{0.4}$$

(3)
Figure 18. Theoretical mass transport mechanisms and diffusion paths that can occur during sintering.

where \( \gamma, \Omega, a, k, T \) and \( t \) are as given before. This equation is based on a bulk diffusion model.

In these derivations, it is always assumed that the particles are monosized spheres, that grain growth does not occur and that the coordination number of the particles remains constant. However, grain growth does occur and particles do rotate, increasing their coordination number as sintering progresses.\(^{73}\) The equations also do not account for the impingement of the necks on each other. Therefore the shrinkage equations developed are only applicable to a few percent (~ 3%) shrinkage during the initial sintering period.

Johnson and Cutler\(^{75}\) developed shrinkage equations based on volume and grain boundary diffusion that extended the useful range of the equations to approximately 5% shrinkage. Their generalized equation is:

\[
\frac{\Delta L}{L_o} = \left( \frac{K \gamma \Omega D}{a^* k T} \right)^m t^n
\]
where $\gamma$, $\Omega$, $a$, $k$, $T$ and $t$ are as given before. $K$, $m$ and $n$ are dependent upon the mass transport mechanism and diffusion path being modelled. The value of $m$ was calculated to be 0.31 and 0.34 for volume and grain boundary diffusion, respectively.

A plot of $\log \left( \frac{\Delta L}{L_o} \right)$ versus log $(t)$ should give a straight line, with the slope of the line varying for the different mass transport mechanisms. Johnson and Cutler tested this equation by sintering compacts of alumina powder.\textsuperscript{76} Instead of a linear relationship between $\log \left( \frac{\Delta L}{L_o} \right)$ and log $t$, they found that the shrinkage curve was composed of three different regions; an initial curved portion, a linear portion and a final curved portion.

The initial curved portion is probably due to particle rearrangement and equilibration to the sintering temperature while the final curved portion due to neck impingement, which decreases sintering rate. The initial curved portion can be eliminated by assuming that there are errors in both the initial length and time measurements. This will be discussed further in a later section.

Model neck growth equations developed by both Kuczynski, Kingery and Berg, Coble and Johnson and Cutler could not be applied to the sintering of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$. Model geometries of spherical, monosized particles are not obtainable with $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ as the particles produced by solid state processes are angular and irregular. In addition, equilibration of the structure to both temperature and oxygen partial pressure cannot be achieved in a short period of time. As the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ changes, sintering mechanisms and kinetics would change. This has been further elaborated in a later section.
1.3 Objectives of Present Study

As mentioned previously, oxygen partial pressure has a significant effect on the solid state sintering behavior of YBa$_2$Cu$_3$O$_{7.8}$. However, the reasons for this effect have not been fully investigated. The present study attempts to relate the sintering kinetics of YBa$_2$Cu$_3$O$_{7.8}$ to oxygen partial pressure, and determine its effect on the sintering kinetics with respect to mass transport mechanisms. This was done by studying the isothermal contraction behavior of YBa$_2$Cu$_3$O$_{7.8}$ in the temperature range 930-960°C with oxygen partial pressures varying from $10^3$ to 1 atmospheres. The change in lattice parameters over this partial pressure range was also studied, in order to evaluate its effect on the sintering behavior.
2 EXPERIMENTAL PROCEDURE

2.1 Powder Preparation

Powders of the ceramic superconducting compound with a nominal composition of YBa$_2$Cu$_3$O$_{7.8}$ were prepared from stoichiometric mixtures of analytical grade Y$_2$O$_3$, BaO$_2$ and CuO. The raw ingredients were dry mixed in a vibratory mixer for several minutes. The mixed powder was repeatedly ground in an agate mortar and pestle to obtain a homogeneous mixture. The raw powder was placed in an alumina crucible and calcined in air at 950°C for 16 hours. The resulting powder, which was black in color, was twice reground and recalcined at 950°C in air. Finally, the powder was calcined at 950°C in flowing oxygen and furnace cooled to 500°C. The powder was held at this temperature for 8 hours under flowing oxygen to ensure maximum oxygen uptake. After this annealing treatment the powder was furnace cooled to room temperature. Figure 19 shows a flow diagram of powder production.

For the purposes of this project, two batches of powder were produced. The first batch, ~200 grams, was used to prepare samples for all the experiments in this project. This was done to ensure that powder chemistry, composition, particle size and distribution were constant from sample to sample. The second batch produced, ~50 grams, was used to repeat several of the experiments. This was done to ensure that the experimental results could be obtained from batch to batch, and were not a function of powder characteristics.

The powder morphology and size distribution were obtained by using a scanning electron microscope (SEM) and a Horiba 700 particle size distribution analyzer.
Figure 19. Flow diagram of the processing steps used to produce YBa$_2$Cu$_3$O$_{7.8}$ powder.
2.2 Sample Preparation

In order to investigate the sintering kinetics in the YBa$_2$Cu$_3$O$_{7.8}$ system, powder compacts were isothermally sintered under various temperatures and oxygen partial pressures. Before a powder compact could be produced, the powder was preprocessed at the desired temperature and oxygen partial pressure for 16 hours. The powder was then air quenched to room temperature and lightly ground in an agate mortar and pestle to obtain a free flowing powder. A quantity of the preprocessed powder was then cold-compacted in a double-action floating die to produce a cylindrical compact. The compaction pressure was 15 MPa. The resulting compact had the dimensions and properties tabulated in Table 4. The initial relative density of the compacts varied as the oxygen content of YBa$_2$Cu$_3$O$_{7.8}$ changed, due to the variation of theoretical density with oxygen content. As the oxygen content decreased, the initial relative density increased from .65 to .68. For a particular oxygen content, initial relative densities varied by less than ± 0.008 p$_{th}$.

YBa$_2$Cu$_3$O$_{7.8}$ is very reactive with platinum, Al$_2$O$_3$, MgO and ZrO$_2$ at high temperatures. It was found that the least reactive crucible material was gold. Therefore, all crucibles and surfaces in contact with YBa$_2$Cu$_3$O$_{7.8}$ at elevated temperatures were constructed from gold.

Table 4. Dimensions and Properties of Powder Compacts

<table>
<thead>
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<th>Sample diameter</th>
<th>9.5 mm (.375 in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample height</td>
<td>6.4 mm (.25 in)</td>
</tr>
<tr>
<td>Sample weight</td>
<td>~2 grams</td>
</tr>
<tr>
<td>Initial density</td>
<td>.65 - .68 p$_{th}$</td>
</tr>
</tbody>
</table>
The preprocessing step was found to be necessary to ensure that the entire compact became equilibrated at the desired temperature and oxygen partial pressure. It was noted that compacts produced from unpreprocessed powders and subsequently sintered in the desired temperature and oxygen pressure developed a two phase structure. The outer layer had equilibrated to the environment while the inner layer had not. In addition, the shrinkage measurements of an unpreprocessed compact would have the combined effects of shrinkage due to sintering, and the change in crystal structure due to the environment.

To investigate the effect of oxygen partial pressure on lattice parameters, no powder preprocessing was required. The as-produced $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ powder was used for all experiments.

2.3 Experimental Apparatus

2.3.1 Isothermal Experiments

The equipment used to obtain isothermal shrinkage curves under various oxygen partial pressures is shown in Figure 20. The setup consists of a vertical tube furnace, an oxygen probe, a linear variable differential transformer (LVDT) and input module, a gas supply and a chart recorder.
Figure 20. Experimental equipment used for isothermal contraction experiments.
2.3.1.1 Vertical Tube Furnace

The vertical tube furnace consists of a 3.9 cm diameter quartz tube, superkanthal heating elements capable of reaching 1600°C and a power supply/temperature control unit. To set the temperature of the furnace, a chromel/alumel thermocouple was inserted inside the quartz tube to a depth corresponding to the position of the compact in the hot zone during sintering. The temperature setting on the furnace control unit, which measured the temperature on the exterior of the quartz tube with a type S (platinum/platinum-10% rhodium) thermocouple, was then adjusted to give the desired temperature on the chromel/alumel thermocouple.

Due to the intermittent nature of the power supply, the temperature varied by approximately two degrees Celsius. For these experiments the temperature at the midpoint of this variation was used as the setpoint.

2.3.1.2 Oxygen Probe

The oxygen partial pressure was measured by a ZrO$_2$-10 at.% CaO oxygen probe which was inserted into the bottom of the quartz tube, Figure 21. The end of the oxygen probe was situated directly below the sample. The oxygen probe also had a number of baffles along its length to provide adequate mixing of the furnace atmosphere.

Prior to use, the outside of the closed end of the ZrO$_2$-10 at.% CaO electrolyte was platinitized by applying a few drops of chloroplatinic acid solution and heating to 800°C. This yielded an adherent platinum deposit on the electrolyte. Platinum wire was then wrapped around this deposit to provide one of the leads for the probe.
Platinum foil was firmly seated in the closed end of the electrolyte. A type S thermocouple was inserted into the electrolyte, making contact with the foil. The platinum wire from the thermocouple provided the other lead required for the probe.

The electromotive force of an oxygen concentration cell is given by:

\[ E = \frac{RT}{4F} \ln \frac{P_{O_2}''}{P_{O_2}'} \]  

where \( F \) is the Faraday constant (23057 calories/volt-equivalent), \( R \) is the gas constant and \( P_{O_2}'' \) and \( P_{O_2}' \) are the oxygen pressures at the cathode and anode, respectively. Ideal gas behavior is assumed (fugacity equals pressure). For these experiments, air was used as the reference oxygen pressure, hence \( P_{O_2}'' = .209 \) atmospheres. Therefore, equation 5 yields:

\[ \ln P_{O_2}' = -1.5654 - \frac{46.418E}{T} \]  

where \( E \) is in millivolts and \( T \) is in degrees Kelvin.

The oxygen probe used in this study was used previously by Professor Mahrotra and was standardized by him. To test the accuracy of this probe several standardized oxygen-argon mixtures were used. It was found that equation 6 could be used to determine the oxygen partial pressure with no correction factors.

To provide various oxygen partial pressures, argon-air mixtures were introduced into the furnace via an inlet in the water cooled copper cap of the oxygen probe. The total pressure in the system did not exceed one atmospheric pressure.
Figure 21. Cross section of tube furnace showing positions of oxygen probe and LVDT assembly for isothermal contraction experiments.
2.3.1.3 Linear Variable Differential Transformer

The apparatus used for obtaining isothermal contraction versus time curves is shown in Figure 22. It consists of a 2.5 cm diameter alumina tube with two 2.4 by 1.5 cm windows cut near the bottom. A 6.5 mm thick alumina platen was placed across the windows to provide a base for the sample. The top of the alumina tube was attached to a water cooled copper sleeve. The LVDT body was connected to the copper sleeve by a threaded cylinder. This allowed the LVDT to be adjusted up to 5 cm vertically. A 60 cm long alumina rod having a diameter of 1.5 mm was inserted into the alumina tube. This rod reached from the alumina platen to the LVDT transducer and supported the iron core required for the LVDT.

The LVDT was connected to a Daytronic type 70 differential transformer input module. The 0.020" full scale range was used for all experiments. The system was initially calibrated using metal strips of known thickness and checked periodically. The input module was connected to a 2 pen Kipp & Zonen strip chart recorder. Both dimensional change and oxygen potential were recorded. The chart recorder was zeroed with respect to the LVDT and oxygen probe before each experiment.

The entire LVDT assembly was mounted on a vertical roller track over the opening of the furnace (see Figure 22). This allowed the assembly to be raised and lowered into the furnace. When the assembly was in the lowered position, the windows cut in the alumina tube were at a depth corresponding to the hot zone of the furnace. A fiberfrax cap was attached to the alumina tube and fitted over the opening in the quartz tube (see Figure 21). This prevented air from entering the furnace atmosphere.
Figure 22. LVDT assembly and arrangement for isothermal contraction experiments.
2.3.2 Quenching Experiments

To determine the effect of oxygen partial pressure on lattice parameters, the furnace arrangement used for isothermal shrinkage experiments was altered. The total LVDT unit was removed from the furnace. The oxygen probe was removed and inserted from the top of the furnace, see Figure 23. A removable plug with a gas inlet was inserted into the bottom of the tube. A small hole was drilled through the copper top of the oxygen probe. This allowed a gold crucible to be suspended in the hot zone of the furnace.

X-ray diffraction analyses were carried out on a Philips X-ray Powder Diffractometer. A copper target with a nickel filter operating at 36 kV, 18 mA was used as the x-ray source. X-ray diffraction patterns were recorded on a chart recorder.
Figure 23. Cross section of tube furnace showing positions of oxygen probe and gold crucible for quenching experiments.
2.4 Experimental Procedure

2.4.1 Isothermal Contraction

To investigate the sintering kinetics of YBa$_2$Cu$_3$O$_{7.5}$, samples produced as described in section 2.2.1 were sintered under various temperatures and oxygen partial pressures.

The sample arrangement for isothermal contraction is shown in Figure 24. The sample was sandwiched between two gold platens, to reduce reactions between the platens and the sample. An alumina platen was placed on the top gold platen to provide some structural support. The alumina rod was placed atop the sample. The combined weight of the platens, rod and iron core was 7.9 grams, resulting in a stress of less than 1 kPa on the sample. The LVDT and chart recorder were calibrated and zeroed.

The LVDT assembly was lowered into the furnace, which was held at a constant temperature and oxygen partial pressure. The linear dimension, L, of the sample during sintering was recorded as a function of time. The total sintering time was 240 minutes. The data was then normalized with respect to the initial length to obtain contraction versus time curves. The initial length value was obtained by adding the final length of the sample to the linear shrinkage measured from the chart.

After sintering, the contraction samples were fractured and the fracture surface was viewed in the SEM. Photomicrographs were obtained to view the morphology of the powder particles in the samples.
Figure 24. Sample arrangement in the LVDT assembly for isothermal contraction experiments.
2.4.2 Quenching

To investigate the change in structure (specifically the lattice parameters) of YBa$_2$Cu$_3$O$_{7.8}$ with respect to oxygen partial pressure, the following procedure was used.

A quantity (~1 gram) of orthorhombic YBa$_2$Cu$_3$O$_{7.8}$ powder was placed in a gold crucible. The crucible was suspended from the top of the furnace into the hot zone by a long wire (see Figure 23). The temperature and oxygen partial pressure in the furnace were held constant.

After 240 minutes, the plug/gas inlet at the bottom of the quartz tube was removed and simultaneously the crucible and powder were dropped into a liquid nitrogen bath placed under the tube. The crucible, filled with liquid nitrogen, was placed in a desiccator which was subsequently evacuated. This prevented water vapor from condensing on the powder as it was returned to room temperature.

The powder was removed from the desiccator and lightly ground in an agate mortar and pestle to obtain a free flowing powder. The powder was immediately put into the x-ray diffraction machine, and the diffraction pattern was obtained. Lattice parameters were determined by a computer program using the characteristic 2Θ values of the diffraction pattern as input.
3 RESULTS

3.1 Powder Characteristics

After synthesis, the YBa$_2$Cu$_3$O$_{7.8}$ powder was characterized with respect to crystallography, mean particle size, size distribution and morphology.

An x-ray diffraction pattern of the as-produced YBa$_2$Cu$_3$O$_{7.8}$ powder between 2Θ values of 20 and 60° was obtained. From the diffraction pattern the powder was identified as orthorhombic. Using the characteristic 2Θ diffraction values as input, a USGS computer program (courtesy of the Department of Geology, University of British Columbia) calculated lattice parameters $a=3.828$ Å, $b=3.897$ Å and $c=11.704$ Å at room temperature. This program uses an iterative, least-square method to determine lattice parameters. No other phase was detected.

A particle size distribution obtained by the Horiba 700 is shown in Figure 25. It is evident that the size distribution is quite broad, with almost all particles less than 68 μm in diameter. The mean diameter is 47 μm with a standard deviation of 20 μm. Two SEM micrographs of the powder particles are shown in Figure 26. It can be seen that the particles are quite angular and irregularly shaped.
Figure 25. a) Particle size distribution and b) cumulative percent greater than distribution of YBa$_2$Cu$_3$O$_{7.8}$ powder.

Figure 26. Scanning electron microscope micrographs of YBa$_2$Cu$_3$O$_{7.8}$ powder (bar = 40 µm).
3.2 Isothermal Contraction

3.2.1 General Observations

To investigate the oxygen partial pressure dependence of the sintering kinetics of YBa$_2$Cu$_3$O$_{7.8}$, isothermal contraction studies were carried out at 930, 945, 955 and 960°C under a range of oxygen partial pressures (1 to 0.001 atmospheres). All of these experiments were repeated several times. Higher temperatures and lower oxygen partial pressures could not be used as they led to incongruent melting of the YBa$_2$Cu$_3$O$_{7.8}$ compound. Similarly, temperatures lower than 930°C were not useful as the amount of shrinkage produced was very small.

The cylindrical contraction specimens, having the dimensions and physical properties shown in Table 4, were used for the sintering experiments. The sample was placed into the LVDT assembly, as shown in Figure 24, and lowered into the furnace. The temperature and oxygen partial pressure of the furnace were set prior to the start of the experiment. The entire assembly was lowered slowly into the hot zone of the furnace. This was done to reduce the thermal shock to the LVDT assembly. Insertion into the furnace was accomplished in approximately two minutes. The samples had relative densities between 0.75 and 0.80 after sintering.

3.2.2 Stages of Contraction

A typical experimental curve showing the dimensional change (height) of the compact from its introduction into the hot zone of the furnace to the end of the experiment is shown in Figure 27. There are three distinct regions evident in this curve. Region I shows expansion of the sample and LVDT assembly as they are heated from room
temperature to the furnace temperature. Region II begins as the sintering of the powder overcomes the thermal expansion. It is this point which is used as the starting time of sintering, $t_0$, and determines the value of $L_0$. This region is characterized by a rapid, nonlinear increase in shrinkage with time.

It should be noted that thermal equilibrium of the apparatus, as measured by the thermocouple attached to the alumina tube of the LVDT assembly (see Figure 21), did not occur until approximately 10 minutes after insertion into the furnace. This occurred in the initial period of Region II. It is presumed that the sample required the same length of time, or more, for thermal equilibration.

The third region shows an approximately linear, steady state increase in shrinkage with time. It is assumed that this region starts once the sample has become fully equilibrated to the temperature and oxygen environment in the furnace. It is this region which is of interest in this study, as it shows the variation of the equilibrium sintering kinetics of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with respect to oxygen partial pressure and temperature.

The shrinkage curves obtained were digitized and then normalized with respect to the compacts' initial length to produce a contraction, $\varepsilon$, versus time, $t$, curve, Figure 28. Only the second and third regions are shown, as Region I is intentionally omitted.

In order to test the reproducibility of the contraction plots, a series of isothermal contraction plots were obtained under identical experimental conditions and these are shown in Figure 29. The results of five experiments at 945°C are shown, three at an oxygen partial pressure of .209 atmospheres and two at a $P_0^2$ of .0024 atmospheres. It can be seen that the reproducibility of these curves at each oxygen partial pressure is very good. All contraction plots and data are included in Appendix I.
Next, a series of contraction experiments were performed at different temperatures while the oxygen partial pressure was held constant. Figure 30 shows contraction curves at the experimental temperatures at an oxygen partial pressure of .209 atmospheres. It is evident that total contraction increases with sintering temperature, and that the two stages of contraction occur at all experimental temperatures.

Similarly, Figure 31 illustrates the effect of oxygen partial pressure on the contraction behavior of samples sintered at 945°C. There doesn't appear to be a monotonic response, the largest contraction occurring for an intermediate oxygen partial pressure (.055 atmospheres) and the lowest contraction encountered both at the highest (.5022 atm) and lowest (.0058 atm) oxygen partial pressures. Again, it is obvious that the two stages of contraction are evident at all experimental oxygen partial pressures.

Plots of log strain (e) versus log time of the data in Figures 30 and 31 are shown in Figures 32 and 33, respectively. It can be seen that there are definitely two stages of contraction. It is felt that in the first stage the complexity of the many processes that are occurring in addition to sintering; eg., thermal equilibration of the sample and apparatus, equilibration of the structure to the oxygen partial pressure and particle rearrangement, preclude the possibility of analyzing the first stage of contraction. During the second stage of contraction, it is assumed that the sample is fully equilibrated and that the increase in contraction is due solely to equilibrium sintering phenomena.
Figure 27. Typical change in height of YBa$_2$Cu$_3$O$_{7.8}$ contraction sample with time from start of experiment. RT indicates the height of the sample at room temperature. The three regions discussed in the text are indicated.
Figure 28. Typical contraction curve obtained from isothermal contraction experiments of YBa$_2$Cu$_3$O$_{7.8}$. Only regions II and III of Figure 27 are shown.
Figure 29. Comparison of contraction curves for duplicate experiments at 945°C. Oxygen partial pressures (in atm.) are shown in the figure.
Figure 30. Contraction curves for \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) samples sintered in air at the temperatures indicated.
Figure 31. Contraction curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ sintered at 945°C in various oxygen partial pressures shown (in atmospheres).
Figure 32. Log contraction - log time plots of data in Figure 30.
Figure 33. Log contraction - log time plots of data in Figure 31.
3.2.3 Oxygen Partial Pressure Dependence

Figures 32 and 33 suggest that the slope of the first stage is relatively temperature independent, while there is an apparent oxygen partial pressure dependence. The slope of this first contraction stage as a function of oxygen partial pressure is plotted as log (slope) versus log (\(P_{O_2}\)), Figure 34. It can be seen that the slope is highest at an intermediate range of oxygen partial pressures and that there is a large amount of scatter in the data during this stage of contraction.

As stated previously, it is felt that equilibrium sintering is the only process occurring during the second stage of sintering. Figures 32 and 33 indicate that this equilibrium sintering stage starts at all experimental temperatures and oxygen partial pressures between 40 and 80 minutes after the start of contraction. To provide the same basis for each experiment, only the data from 80 minutes to the end of sintering is analyzed for all contraction samples.

From Figure 31 it is obvious that oxygen partial pressure does have an effect on contraction. To investigate the effect of oxygen partial pressure on the sintering of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\), the slope of the steady state region, from 80 to 240 minutes, is obtained from the contraction curve. This slope is equal to the steady state contraction rate, \(\dot{e}\), of the compact.

If the contraction rate is dependent upon the oxygen partial pressure, that is \(\dot{e} = f(P_{O_2})\), and if it is assumed that a power law relationship exists between these parameters then:

\[
\dot{e} \propto P_{O_2}^a
\]  
(7)
where \( n \) is a constant, should be valid. A plot of \( \log(\epsilon) \) versus \( \log(P_0^2) \) would then give a straight line with slope \( n \). Figures 35, 36 and 37 show \( \log(\epsilon) \) versus \( \log(P_0^2) \) for 930, 945 and 955°C, respectively.

From these figures it can be seen that oxygen partial pressure does have an effect on the steady state contraction rate of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \). There is a maximum in contraction rate at some critical oxygen partial pressure, \( P_0^{\text{CRIT}} \). Contraction rate decreases with oxygen partial pressure both above and below \( P_0^{\text{CRIT}} \). It can be seen that for oxygen partial pressures above \( P_0^{\text{CRIT}} \), \( \log(\epsilon) \) decreases more or less linearly with increasing \( \log(P_0^2) \) with a slope of approximately -1/6 for all three temperatures. This peak in contraction rate occurs at a \( P_0^2 \) of 0.050, 0.063 and 0.079 atmospheres for 930, 945, and 955°C, respectively. Using these values in either Figure 14 or equation 1, the oxygen content at this peak was calculated to be approximately 6.2 for all temperatures.

A gradual decrease of \( \log(\epsilon) \) with decreasing \( \log(P_0^2) \) below \( P_0^{\text{CRIT}} \) is also observed. The slope of the line drawn through the experimental data changes slightly from one temperature to another, but is close to a value of +1/6.

The relationship between contraction rate and oxygen partial pressure at 960°C is shown in Figure 38. Compared to the relationship at 945°C, it appears that the contraction rate at 960°C is independent of oxygen partial pressure.

The results of samples produced from the second batch of powder are shown in Figure 39. Samples were sintered at 945°C under various oxygen partial pressures. It can be seen that the approximate -1/6 and +1/6 relationships between \( \log(\epsilon) \) and \( \log(P_0^2) \) above and below \( P_0^{\text{CRIT}} \) are also valid for the second batch of powder.
Figure 34. Log-log plot of the initial slope of the contraction curves versus $P_0^2$ (atm.) for samples sintered at 945°C.
Figure 35. Log $\dot{\varepsilon}$ - log $P_0$ plots for YBa$_2$Cu$_3$O$_{7.8}$ samples sintered at 930°C showing a maximum in contraction rate at some $P_0$, with decreasing contraction rates above and below this oxygen partial pressure.
Figure 36. Log $\varepsilon$ - log $\text{PO}_2$ plots for YBa$_2$Cu$_3$O$_{7.5}$ samples sintered at 945°C showing a maximum in contraction rate at some $\text{PO}_2$, with decreasing contraction rates above and below this oxygen partial pressure.
Figure 37. Log $\dot{\varepsilon}$ - log $P_0^2$ plots for YBa$_2$Cu$_3$O$_{7.5}$ samples sintered at 955°C showing a maximum in contraction rate at some $P_0^2$, with decreasing contraction rates above and below this oxygen partial pressure.
Figure 38. Comparison of log $\dot{e}$ - log $P_{O_2}$ plots for YBa$_2$Cu$_3$O$_{7.5}$ samples sintered at 945 and 960°C. Contraction rate appears to be independent of oxygen partial pressure at 960°C.
Figure 39. Log $\varepsilon$ - log $P_{O_2}$ plots for YBa$_2$Cu$_3$O$_{7.8}$ samples from the second batch of powder, sintered at 945°C. The maximum in contraction rate at some $P_{O_2}$ is evident.
3.2.4 Temperature Dependence

The temperature dependence of the contraction rate at a constant oxygen partial pressure above $P_{O_2}^{Crit}$ was investigated by plotting the value of $\ln (\dot{e})$ at two oxygen partial pressures (1 and 0.10 atmospheres) versus reciprocal temperature, as shown in Figure 40. This figure also shows the temperature dependence of contraction rates at two oxygen partial pressures below $P_{O_2}^{Crit}$ (0.025 and 0.0063 atmospheres). It can be seen that the data obtained for 960°C, which is independent of oxygen partial pressure, does not fit into the trend established by the other temperatures. Lines can be drawn through the data for each oxygen partial pressure for 930-955°C. From the slope of the lines and using the Arrhenius equation:

$$\dot{e} = KE^{-\frac{E}{RT}}$$

the activation energy $E$ can be calculated. The activation energy required for the sintering process for oxygen partial pressures above $P_{O_2}^{Crit}$ is estimated to be 176±12 kJ/mole for both 1 and 0.1 atmospheres of oxygen. For oxygen partial pressures below $P_{O_2}^{Crit}$, the activation energy required for the sintering process is estimated to be 130±10 kJ/mole for both 0.0063 and 0.025 atmospheres of oxygen.
Figure 40. Arrenhius plot to calculate the activation energy of sintering for YBa$_2$Cu$_3$O$_{7.8}$. 
3.2.5 Microstructure of the Sintered Samples

After sintering the fracture surface of the contraction samples was viewed in the scanning electron microscope. SEM micrographs of samples sintered at 930, 945, 955 and 960°C under various oxygen partial pressures are shown in Figures 41, 42, 43 and 44, respectively.

From these figures it can be seen that the sintered particles retain their irregular shape during the course of sintering. The particles sintered at 960°C show a reduction in their angularity and somewhat smooth, rounded interparticle contacts can be seen. This is also evident to some degree in the samples sintered in the lowest oxygen partial pressures at other temperatures. The rest of the samples show angular particles with sharp edges and interparticle contacts. The reduction in angularity and smooth interparticle contacts can be considered as an indication of the presence of a liquid phase during sintering. Therefore, liquid phases were most likely present at all oxygen partial pressures for the samples sintered at 960°C.

Another feature to be noted in these figures is that the particle size at all temperatures and oxygen partial pressures is relatively constant. The contribution of particle growth to sintering should, therefore, be insignificant.
Figure 41. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7.8}$ contraction samples sintered at 930°C in an oxygen partial pressure of a)0.5924 atm b)0.0049 atm (bar=20 μm).
Figure 42. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7-\delta}$ contraction samples sintered at 945°C in an oxygen partial pressure of a) 0.5022 atm b) 0.0323 atm (bar=20 μm).
Figure 42. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7.5}$ contraction samples sintered at 945°C in an oxygen partial pressure of 0.0058 atm (bar=20 μm).
Figure 43. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7-\delta}$ contraction samples sintered at 955°C in an oxygen partial pressure of a)0.8791 atm b)0.0271 atm (bar=20 μm).
Figure 43. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7.8}$ contraction samples sintered at 955°C in an oxygen partial pressure of c) 0.0048 atm (bar=20 µm).
Figure 44. SEM micrograph of fracture surface of YBa$_2$Cu$_3$O$_{7.8}$ contraction samples sintered at 960°C in an oxygen partial pressure of a) 0.4785 atm b) 0.0295 atm (bar=20 µm).
3.3 Quenching

To determine the effects of oxygen partial pressure on the structure of YBa$_2$Cu$_3$O$_{7-8}$, powder samples were introduced into the furnace as shown in Figure 23. The temperature and oxygen partial pressure of the furnace were set prior to insertion and held constant during the experiment. After the proper heat treatment the powder was quenched by immersion in liquid nitrogen.

An X-ray diffraction pattern obtained from a quenched specimen is shown in Figure 45. This is a typical diffraction pattern for the tetragonal structure of YBa$_2$Cu$_3$O$_{7-8}$. X-ray diffraction patterns were obtained for all samples equilibrated at different oxygen partial pressure at 945°C. The 2Θ values (accuracy ±0.04°) from 20 to 60° for each diffraction pattern was used to determine lattice parameters. All characteristic 2Θ values for tetragonal YBa$_2$Cu$_3$O$_6$ are included in Appendix II. The lattice parameters were calculated by the method described in section 3.1. It is estimated that the value of the a-lattice parameter is accurate to within three decimal places (±0.001), and the value of the c-lattice parameter within two decimal places (±0.01).

Figures 46 and 47 show the a- and c-lattice constants versus oxygen partial pressure, respectively. It can be seen that the value of a- decreases with decreasing oxygen partial pressure while that of c- increases. It should be noted that both the a- and c-lattice parameters do not experience a linear change with respect to oxygen partial pressure. As the oxygen partial pressure is decreased, the rate of change in the lattice parameters decreases as well. The unit cell data are included in Appendix III.

The unit cell volume as a function of oxygen partial pressure is shown in Figure 48. This was calculated from the lattice parameters obtained from the computer program. The
unit cell volume decreases as oxygen partial pressure decreases. Similar to the a-lattice parameter, the rate of change in unit cell volume decreases as the oxygen partial pressure decreases.
Figure 45. Typical x-ray diffraction pattern of tetragonal YBa$_2$Cu$_3$O$_{7-8}$ between 2$\theta$ values of 20 and 60°.
Figure 46. Variation of the a-lattice parameter of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ with oxygen partial pressure at 945°C.
Figure 47. Variation of the c-lattice parameter of YBa$_2$Cu$_3$O$_{7-\delta}$ with oxygen partial pressure at 945°C.
Figure 48. Variation of the unit cell volume of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ with oxygen partial pressure at 945°C.
4 DISCUSSION

4.1 General Observations

4.1.1 Contraction Behavior

As mentioned earlier, all contraction curves obtained during sintering of YBa$_2$Cu$_3$O$_{7.5}$ have two stages of contraction occurring during sintering. In the first stage, contraction is rapid and nonlinear. After a period of time, the rate of contraction decreases and an approximately constant, steady state increase in contraction with time is observed.

Theoretical sintering equations (see section 1.2) predict that a plot of logarithm contraction versus logarithm time should give a straight line, the slope of which is dependent on the mechanism of mass transport that is operating. However, from Figures 32 and 33, in which plots of log $e$ versus log $t$ for YBa$_2$Cu$_3$O$_{7.5}$ samples sintered at one oxygen partial pressure with varying temperatures, and at one temperature for various oxygen partial pressures are shown, it is evident that there are two distinct contraction regions.

During the first stage of contraction, several processes are known to be occurring, as mentioned before. These include thermal equilibration of the sample and apparatus, structural equilibration of YBa$_2$Cu$_3$O$_{7.5}$ to the furnace environment, particle rearrangement due to anisotropic stresses at the neck regions and shrinkage due to sintering. These concurrent processes make this stage of contraction difficult to analyze. One of these difficulties is shown in Figure 34, which shows that the slope of the first stage of contraction varies widely with respect to oxygen partial pressure. Consequently, no attempt has been made to analyze the first stage of contraction.
It should be noted that structural equilibration of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ compacts was necessary even though the powder was preprocessed before sintering. Due to the furnace arrangement, the preprocessed powder could not be quenched in a manner similar to that used to obtain the equilibrated powder for lattice parameter determinations. The preprocessed powder was removed from the furnace environment ($T$, $P_{O_2}$) and cooled to room temperature in air. This required approximately 3 minutes. During this time interval, the preprocessed powder picks up oxygen. The oxygen content of the preprocessed powder, as indicated by the value of $x$ in $\text{YBa}_2\text{Cu}_3\text{O}_x$, was approximately 6.5 at room temperature, while the oxygen content of the powder at 930 - 960°C was less than 6.3 for all oxygen partial pressures used in the contraction experiments. Therefore structural equilibration of the contraction samples was essential.

The preprocessing step was, however, necessary to ensure that the entire contraction sample was equilibrated to the oxygen environment. Contraction samples produced from as-produced orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ developed a two phase structure when sintered in low oxygen partial pressures. The outer portion of the contraction sample had equilibrated to the oxygen environment while the inner portion had not.

During the second stage of contraction, it is assumed that the $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ sample is fully equilibrated and that shrinkage is occurring only by an equilibrium sintering mechanism. Therefore, only the contraction versus time data during the second stage of contraction is analysed in order to evaluate the sintering kinetics of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$.

The multiple factors affecting the first stage of contraction may not be occurring to the same extent or at the same rates for all experimental conditions. This is evident in Figures 32 and 33, which indicates that the start of the second stage of contraction does not occur at the same time for different temperatures and oxygen partial pressures. However,
it can be observed that the second stage of contraction is occurring at all experimental condition after a time of 80 minutes. Therefore, analysis of sintering kinetics for all samples used only the data from 80 minutes to the end of the experiment.

The value of 80 minutes was used for all samples to provide a common analytical basis for all experimental conditions. For those samples with a linear relationship between \( \log e - \log t \) at shorter times, the exclusion of this data will have no effect on subsequent analysis, as it is a linear relationship.

4.1.2 Temperature Effects

As shown previously, at a given oxygen partial pressure the total contraction (Figure 30) increases as the sintering temperature is increased. Sintering requires atomic transport for densification for solid state sintering. Any change in vacancy concentration in the sintering system (which affects atomic transport) should produce a change in the sintering kinetics. If the sintering kinetics are independent of vacancy concentration, then it is unlikely that solid state sintering is controlling the sintering behavior.

The oxygen content of a \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) sample at a given temperature decreases with decreasing oxygen partial pressure. This can be seen in Figure 14, or by analyzing equation 1. Therefore the oxygen vacancy concentration in \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) increases with decreasing oxygen partial pressure.

Figures 35 to 37 show that the sintering kinetics of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) between 930 and 955°C are dependent on the oxygen partial pressure, and therefore, dependent on oxygen vacancy concentration. This indicates that solid state sintering is controlling the densification behavior of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.8} \) at these temperatures.
Figure 38 shows, however, that the sintering kinetics of YBa$_2$Cu$_3$O$_{7.8}$ at 960°C are relatively independent of oxygen partial pressure. Consequently, the densification behavior at 960°C is most likely governed by a mechanism other than solid state. As the formation of liquid phases is more likely as the temperature is increased, it is felt that a liquid phase is responsible for the densification behavior of YBa$_2$Cu$_3$O$_{7.8}$ at 960°C.

The presence of a liquid phase at 960°C for all oxygen partial pressures is supported by the SEM micrographs of the fracture surfaces of the contraction samples, Figure 44. It can be seen that the powder particles have somewhat lost their angularity and that interparticle contact regions and pores are smooth and rounded. In contrast, SEM micrographs of the fracture surface of compacts sintered at lower temperatures show particles retaining their angularity and sharp, angular interparticle contacts.

It should be reiterated that the formation of a liquid phase during sintering of YBa$_2$Cu$_3$O$_{7.8}$ is not desired, as the superconducting properties are degraded. It was not the intention of this experimental program to produce liquid phases during sintering.

One may also notice that the contraction rates of samples sintered at 960°C are of the same order of magnitude as the peak values at 945°C (Figure 38), and that the total contraction at 960°C is of the same magnitude as the other temperatures (Figure 30). It seems intuitive that the presence of a liquid phase should produce enhanced densification when compared to solid state sintering. This may be an indication that the quantity of liquid formed is small at this temperature. Several samples were sintered under conditions which formed large quantities of liquid phases (970°C, PO$_2$=.0005 atmospheres). The total contraction was up to 4 times larger than those for samples sintered at 960°C. The contraction curve was also substantially different, with a very large, rapid, linear increase in contraction with time, followed by a sharp transition to a slowly increasing contraction.
rate. In addition, the cylindrical sample had slumped and become barrel shaped. As the total contraction, contraction curve characteristics and sample stability at 960°C were similar to those obtained for lower temperatures, the quantity of liquid phase present at 960°C must be small.

4.1.3 Oxygen Partial Pressure Effects

Figures 35 to 37 show the effects of oxygen partial pressure on the contraction rate at 930, 945 and 955°C, respectively. Starting at a high oxygen partial pressure, it can be seen that the contraction rate increases with decreasing oxygen partial pressure, up to some critical oxygen partial pressure, $P_{O_2}^{\text{CRIT}}$. As the oxygen partial pressure is further reduced, the contraction rate decrease from the value at $P_{O_2}^{\text{CRIT}}$. This may be an indication that the sintering kinetics are affected by some other factor as the oxygen partial pressure is further reduced.

A 'best-fit' straight line has been drawn through the points in Figures 35 to 37. It can be seen that there is some scatter in the data for these figures. This scatter may be due to a combination of experimental errors: (i) accuracy of oxygen partial pressures measurements, (ii) estimation of the initial length of the compact, and (iii) sample temperature. Another factor may be that the sample, especially at the lower $P_{O_2}$’s, was not fully equilibrated to the oxygen partial pressures. This may have led to small errors in determining the contraction rates.

Structural changes also occur as the oxygen partial pressure is reduced. These changes will be reviewed in further detail. At all experimental temperatures and oxygen partial pressures the $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples are in the tetragonal phase. For samples under 1
atmosphere of oxygen, the oxygen content, $x$, is approximately 6.3 at all experimental temperatures. As the oxygen partial pressure is reduced, to approximately 0.001 atmospheres, the oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_x$ falls to a value close to $x=6.0$.

As can be seen in Figure 6b and further illustrated in Figure 49, there are three possible sites for oxygen ions in the tetragonal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$. These sites are labeled O(1), O(2), and O(4) as shown in Figure 49. Yan et al.\textsuperscript{79} have studied the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.54}$ by neutron diffraction and have found that the site occupation frequency for O(4), O(2) and O(1) are .99, 1.00 and .30, respectively. Therefore, as the oxygen partial pressure is reduced, and the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ is lowered, only those oxygen atoms in the O(1) sites are lost. In the $\text{YBa}_2\text{Cu}_3\text{O}_6$ structure the O(1) sites should be completely empty. Yan et al.\textsuperscript{79} found that the site occupation frequency for all non-oxygen sites in $\text{YBa}_2\text{Cu}_3\text{O}_{6.54}$ was equal to 1.00.

Figure 49. a) Tetragonal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ b) Detail of the $z=0$ plane showing oxygen sites.[26]
4.2 Analysis of Contraction Data Using Johnson and Cutler Procedure

Johnson and Cutler\textsuperscript{75,76} studied the initial stage sintering kinetics of alumina by measuring the isothermal shrinkage of compacts sintered at various temperatures in air. Their methods have been found to be the most suitable for analysis of the data in the present study. This was done in an attempt to gain an insight into the sintering kinetics of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta}. It should be noted that the Johnson and Cutler equation does not take into account explicitly the effects of oxygen partial pressure on sintering kinetics.

Johnson and Cutler\textsuperscript{75} developed neck growth equations which are similar to those of Kuczynski\textsuperscript{71}. From the neck growth equations Johnson and Cutler also developed a shrinkage equation. The generalized equation of shrinkage:

\[
\frac{\Delta L}{L_o} = \left( \frac{K\gamma\Omega D}{a^nkT} \right)^m t^n
\]

where the variables are as given in section 1.2.

This equation predicts that a logarithm \(\frac{\Delta L}{L_o}\) - logarithm time plot is a straight line with slope \(m\), which is characteristic of the mechanism of material transport. Johnson and Cutler\textsuperscript{75} found that the apparent slopes of experimental log \(\frac{\Delta L}{L_o}\) - log \(t\) varied for different runs. They attributed these variations to errors in determining the initial length of the compact and the start time of sintering.

During the second stage of contraction YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta} sintered in air at various temperatures, Figure 32, the slopes of log \(\frac{\Delta L}{L_o}\) versus log time are all approximately equal to 1/3. According to the derivations of Coble\textsuperscript{74} and Johnson and Cutler,\textsuperscript{75} the sintering could be attributed to bulk or grain boundary diffusion. Kingery\textsuperscript{80} also derived an equation for liquid phase sintering in which the exponent of time is 1/3.
To analyze errors in shrinkage and time measurements, Johnson and Cutler\textsuperscript{76} plotted the length at any time, $L$, of an alumina compact as a function of $t^m$. An $m$ value of 0.31 was used, as this was predicted for one of their models. This plot should theoretically give a straight line. It was found that each curve could be straightened by subtracting a time correction, $\delta t$, from the time at each point on the curve. When the curves were thus straightened, it was found that a length correction, $\delta L$, was also needed to have the fractional shrinkage, $\left(\frac{L}{L_0}\right)$, start at a value of 1.00 at $t=0$.

The length correction probably represents the amount of compact shrinkage required before the powder could be described by the geometrical conditions of the sintering theory. The time correction represents the time to heat the specimen to constant temperature or the time needed to reach the steady-state conditions described by the $\delta L$ corrections. The time correction has little effect on the contraction data at long sintering times, and doesn't affect the slope of the curve. The $\delta L$ correction is more significant at lower compactions and affects the slope of the $L - t^m$ curve. After applying these corrections to experimental data, linear $\frac{L}{L_0} - t^m$ curves were obtained, as predicted by theory.

Figure 50 shows plots of $\left(\frac{L}{L_0}\right)$ versus $t^{1/3}$ for the data in Figure 32. Only the contraction data for times greater than 80 minutes was used. It was felt that these times were large enough to negate the effect of a time correction, so it was not applied. This is supported by the fact that the lines are linear. If a $\delta t$ correction was necessary the lines would be curved.

The $\delta L$ corrections were obtained by extrapolating the lines in Figure 50 back to $t=0$ minutes. The difference between $\left(\frac{L}{L_0}\right)$ and 1.0 is taken as $\delta L$. An adjusted length, $L_e$, is then calculated by subtracting $\delta L$ from the original length of the compact. Plots of $\left(\frac{L}{L_0}\right)$ versus $t^{1/3}$ can then be drawn, as shown in Figure 51.
The slopes of the lines in Figure 51 are given by:\textsuperscript{76}

\[ \text{slope} = -\left( \frac{K'\Omega D}{a^n kT} \right)^{1/3} = -\left( \frac{K'D}{T} \right)^{1/3} \]  \hspace{1cm} (9)\)

where the variables are as per equation 3. Thus, the activation energy can be obtained by plotting 3*\( \log (\text{-slope}) \) as a function of reciprocal temperature, Figure 52. The data points are the average slopes obtained from several duplicate runs. The error bars indicate the range in slopes obtained from these runs. It can be seen that the data for the runs at 960°C do not follow the trend established for the lower temperatures. The activation energy was calculated to be 191±10 kJ/mole.
Figure 50. Fractional shrinkage versus $t^{1/3}$ for the compaction data in Figure 32.
Figure 51. Corrected fractional shrinkage versus $t^{1/2}$ for the data in Figure 50.
Figure 52. Activation energy plot for the sintering of YBa$_2$Cu$_3$O$_{7.5}$. 
4.3 Activation Energies

The activation energy for sintering of YBa$_2$Cu$_3$O$_{7.8}$ above PO$_2^{\text{CRIT}}$ has also been calculated by another method. As shown in the previous section, the activation energy as determined by the Johnson and Cutler technique for YBa$_2$Cu$_3$O$_{7.8}$ sintered in air was 191±10 kJ/mole. As shown in Figure 40, the activation energy as determined from the contraction rates was 176±12 kJ/mole. These values are in good agreement. For oxygen partial pressures below PO$_2^{\text{CRIT}}$, an activation energy of 130±10 kJ/mole was obtained.

Very few researchers have reported activation energies or diffusion coefficients for YBa$_2$Cu$_3$O$_{7.5}$. There seems to be a large range of values obtained for different researchers. Hedge$^{81}$ has found that the activation energy for oxygen desorption above 470°C is 54 kcal/mole (226 kJ/mole). Brabers et al.$^{29}$ also studied oxygen desorption at elevated temperatures and calculated an activation energy of 1.3 eV (127 kJ/mole). This same value of activation energy was obtained by Strauven et al.$^{82}$ Gallagher et al.$^{19}$ have reported an activation energy of 199 kJ/mole for oxygen desorption by TGA analysis. It is not known if these discrepancies are due to the different measuring techniques, samples or other unknown factors.

Mitchell et al.$^{83}$ report a diffusion coefficient of approximately 10$^{-14}$ cm$^2$/s for bulk diffusion of $^{18}$O obtained for single crystals by oxygen exchange and subsequent depth profiling by ion-beam techniques. A value of 5x10$^{-8}$ cm$^2$/s has been reported$^{84}$ for diffusion of oxygen in polycrystalline materials at 550°C, maybe representing the grain boundary diffusion coefficient.
4.4 Possible Sintering Mechanisms

As shown previously, the contraction rate during sintering of YBa$_2$Cu$_3$O$_{7.5}$ between 930 and 955°C is dependent on the oxygen partial pressure. There is a maximum in contraction rate at some oxygen partial pressure, $P_{O_2}^{CRIT}$, with decreasing contraction rates both above and below this oxygen partial pressure. This indicates the possibility that there are two mechanisms responsible for this behavior, one operating above $P_{O_2}^{CRIT}$ and one operating below $P_{O_2}^{CRIT}$. Therefore the analysis of this behavior will be broken up into two parts.

4.4.1 Vacancy Diffusion Mechanism, $P_{O_2} > P_{O_2}^{CRIT}$

As the oxygen partial pressure is increased from $P_{O_2}^{CRIT}$ to 1 atmosphere, the contraction rate decreases. The decrease in log $\dot{\epsilon}$ with log $P_{O_2}$ is linear with a slope of -1/6 for all experimental temperatures. Concurrently, the oxygen content increases, and the oxygen vacancy concentration decreases, as $P_{O_2}$ is raised. This implies that the oxygen vacancy concentration is having an effect on the contraction rate of YBa$_2$Cu$_3$O$_{7.5}$.

As the oxygen partial pressure is increased, gaseous oxygen is combining with the oxygen vacancies in YBa$_2$Cu$_3$O$_{7.5}$ to form oxygen ions in the lattice by the following reaction:

\[
\frac{1}{2}O_2(g) + VO^{2-} + 2\Theta = O_i^{2-}
\]  

where $VO^\Theta$ represents an oxygen vacancy and $\Theta$ represents an electron.

The equilibrium coefficient, $K$, is given as:

\[
K = \frac{[O_i^{2-}]}{P_{O_2}^{1/2}[VO^{2-}][\Theta]^2}
\]
As the activity of the lattice oxygen is 1, and that the concentration of oxygen vacancies is 1/2 the concentration of electrons ([VO^{2-}] = \frac{1}{2}[\Theta]), equation 11 can be rewritten as:

\[ K = \frac{1}{C_1 PO_2^{1/2}[VO^{2-}]^3} \]  \hspace{1cm} (12)

where \( C_1 \) is some constant. By rearrangement it is found that:

\[ [VO^{2-}]^3 = K_1 PO_2^{-1/2} \]  \hspace{1cm} (13)

or:

\[ [VO^{2-}] = K_2 PO_2^{-1/6} \]  \hspace{1cm} (14)

where \( K_1 \) and \( K_2 \) are some constants. If the oxygen ion diffusion is controlling the sintering of the YBa$_2$Cu$_3$O$_{7-\delta}$ compound, any change in oxygen vacancy concentration would affect the contraction rate. That is:

\[ \dot{\varepsilon} \propto PO_2^{-1/6} \]  \hspace{1cm} (15)

The plots in Figures 35 to 37 support this argument. It is not surprising that the contraction rate is affected by oxygen partial pressure. Starting at \( PO_2^{\text{CRIT}} \), as the oxygen partial pressure is increased the oxygen vacancy concentration decreases, and this lowers the densification rate. The values obtained for the activation energy for sintering are also in good agreement with those for the activation energy for oxygen diffusion. This supports the argument that sintering at oxygen partial pressures above \( PO_2^{\text{CRIT}} \) is occurring by an oxygen diffusion mechanism.

**4.4.2 Possible Mechanisms, \( PO_2 < PO_2^{\text{CRIT}} \)**

The decrease in contraction with decreasing oxygen partial pressures below \( PO_2^{\text{CRIT}} \) is unexpected. It is known that the oxygen vacancy concentration is increasing as \( PO_2 \)
decreases, therefore, according to the vacancy diffusion mechanism presented in the previous section, an increase in contraction rate with decreasing PO\(_2\) was expected. This implies that either a different mechanism is operating for oxygen partial pressures below PO\(_2\)\text{CRIT}, or that vacancy diffusion is somehow being inhibited. Several possible factors explaining the contraction rate behavior below PO\(_2\)\text{CRIT} are presented below.

4.4.2.1 Mechanisms for \(\dot{\varepsilon} \propto P O_2^{1/6}\)

As the slope of the log (\(\dot{\varepsilon}\)) - log (PO\(_2\)) curve is approximately 1/6 at all temperatures for oxygen partial pressures below PO\(_2\)\text{CRIT}, mechanisms which would produce sintering rates proportional to \(PO_2^{1/6}\) have been considered.

4.4.2.1.1 Copper Vacancy Diffusion Mechanism

As the oxygen content in the YBa\(_2\)Cu\(_3\)O\(_7\) structure increases, the average oxidation state of copper increases as well. The Cu-O bond is highly covalent, and this can lead to charge disproportionation between Cu\(^{2+}\) and Cu\(^{3+}\). This can occur by the following reaction:

\[
Cu_i^{2+} + \frac{1}{2} O_{2g} = 2Cu^{3+} + O_i^{2-} + VCu^{2+}
\]  

(16)

where \(VCu^{2+}\) represents a copper ion vacancy.

The equilibrium coefficient, \(K_3\), is given by:

\[
K_3 = \frac{[Cu^{3+}]^2 [VCu^{2+}] [O_i^{2-}]}{PO_2^{1/2} [Cu_i^{2+}]} \]  

(17)
As the activity of Cu\(^{2+}\) and O\(^2-\) ions in the lattice are equal to 1.0, and the concentration of Cu\(^{3+}\) is equal to twice the vacancy concentration of Cu\(^{2+}\) ([Cu\(^{3+}\)] = 2[VCu\(^{2+}\)]) equation 17 can be rewritten as:

\[
K_3 = \frac{C_2[VCu^{2+}]^3}{PO_2^{1/2}}
\]

where \(C_2\) is some constant. By rearrangement it is found that:

\[
[VCu^{2+}]^3 = K_4PO_2^{1/2}
\]

or:

\[
[VCu^{2+}] = K_5PO_2^{1/6}
\]

where \(K_4\) and \(K_5\) are some constants.

If the copper ion diffusion is controlling the sintering of YBa\(_2\)Cu\(_3\)O\(_{7.8}\) below \(PO_2^{CRRT}\), any change in the concentration of \(VCu^{2+}\) would affect the contraction rate. That is:

\[
\dot{\varepsilon} \approx PO_2^{1/6}
\]

However, by a simple charge balance it can be seen that for oxygen contents below \(x=6.5\) in YBa\(_2\)Cu\(_3\)O\(_x\), the average oxidation state for copper is less than 2, while for oxygen contents above \(x=6.5\) the average oxidation state for copper is greater than two. At an oxygen content of \(x=6.5\) the average copper oxidation state equals 2. This indicates that for \(x < 6.5\), only Cu\(^{1+}\) and Cu\(^{2+}\) are present. In fact, the formula for YBa\(_2\)Cu\(_3\)O\(_6\) should be written as YBa\(_2\)Cu\(^{1+}\)Cu\(^{2+}\)O\(_6\) where Cu\(^{2+}\) resides in the CuO\(_2\) sheets and Cu\(^{1+}\) resides in the O-Cu-O sticks along the c-axis.\(^8\) As the oxygen content is increased above \(x=6.5\) the oxidation states change to Cu\(^{2+}\) and Cu\(^{3+}\).

As all oxygen contents in YBa\(_2\)Cu\(_3\)O\(_x\) below \(PO_2^{CRRT}\) are less than \(x=6.5\), the likelihood of producing Cu\(^{3+}\) ions in the YBa\(_2\)Cu\(_3\)O\(_{7.8}\) structure by the above
mechanism is minimal. Also, the copper ion site occupation has been shown to be 1.0 at \( x = 6.54 \). Therefore, the concentration of copper ion vacancies must be very small and unlikely to contribute to the sintering of \( \text{YBa}_2\text{Cu}_3\text{O}_{7.5} \).

4.4.2.1.2 Positive Hole Mechanism

As the oxygen content is increased, positive holes may be created in addition to \( \text{Cu}^{2+} \) vacancies. This can be seen by the substituting the following reaction:

\[
\text{Cu}^{3+} = \text{Cu}^{2+} + \Theta
\]

into:

\[
\text{Cu}_i^{2+} + \frac{1}{2} \text{O}_{2(g)} = 2\text{Cu}^{3+} + \text{O}_i^{2-} + (\text{VCu}^{2+})''
\]

(23)

to obtain:

\[
\frac{1}{2} \text{O}_{2(g)} = \text{Cu}_i^{2+} + \text{O}_i^{2-} + 2 \Theta + (\text{VCu}^{2+})''
\]

(24)

where \( \Theta \) represents a positive hole, and \( (\text{VCu}^{2+})'' \) represents a copper vacancy.

The equilibrium coefficient, \( K_6 \), is given by:

\[
K_6 = \frac{[\text{VCu}^{2+}][\text{Cu}_i^{2+}][\text{O}_i^{2-}][\Theta]^2}{\text{PO}_2^{1/2}}
\]

(25)

As the activity of the lattice ions is 1, and the concentration of holes is equal to twice the concentration of \( \text{VCu}^{2+} \) ([\( \Theta \)] = 2[\( \text{VCu}^{2+} \)]) equation 25 can be rewritten as:

\[
K_6 = \frac{C_3[\Theta]^3}{\text{PO}_2^{1/2}}
\]

(26)

where \( C_3 \) is some constant. By rearrangement it is found that:

\[
[\Theta]^3 = K_7\text{PO}_2^{1/2}
\]

(27)
or:

$$[\Phi] = K_8 P O_2^{16}$$  \hspace{1cm} (28)

where $K_7$ and $K_8$ are some constants.

The production of positive holes as the oxygen content increases has been established by Yoo.\textsuperscript{31} Yoo studied the thermoelectric power of YBa$_2$Cu$_3$O$_{7-\delta}$ as a function of oxygen partial pressure at various temperatures. Thermoelectric power isotherms versus log P$_2$ are shown in Figure 53. It can be seen that there is a maximum in thermoelectric power for some P$_2$, with decreasing thermoelectric power above and below this oxygen partial pressure. This is similar to the results of log \( \dot{\varepsilon} \) - log P$_2$ obtained in this study. By plotting thermoelectric power versus oxygen content, x, it can be seen that the thermoelectric power above an oxygen content of x~6.35 is temperature-insensitive, Figure 54. This is only possible when charge carriers execute correlated hole-hopping. Yoo\textsuperscript{31} postulates that this hole hopping in YBa$_2$Cu$_3$O$_x$ occurs between Cu$^{2+}$ and Cu$^{3+}$.

While it can be shown that $[\Phi] \approx P O_2^{1/6}$, the probability that contraction rate is influenced by changes in hole concentration is small. Solid state sintering mechanisms require material transport for densification to occur. Movement of positive holes (or hole hopping) are not capable of transporting material. In addition, Cu$^{3+}$ ions should not be present in YBa$_2$Cu$_3$O$_x$ for oxygen partial pressures below PO$_2^{\text{CRIT}}$, as explained previously. Therefore, it appears that the contraction rate, $\dot{\varepsilon}$, dependence on PO$_2$ below PO$_2^{\text{CRIT}}$ is due to some other factor.
4.4.2.2 Lattice Strain Effect

As shown in Figure 48, the unit cell volume decreases as the oxygen partial pressure decreases. By using equation 1, a unit cell volume versus oxygen content, \( x \), can be obtained, Figure 55. It can be seen that the rate of change in unit cell volume decreases as the oxygen content decreases. It could be argued that the unit cell volume should decrease linearly with decreasing oxygen content because of mass loss, as shown by the solid line in Figure 55. It appears that this linear relationship between \( x \)
and unit cell volume is valid at oxygen contents above approximately 6.2. As the oxygen content is reduced below x=6.2, the discrepancy between the expected and observed unit cell volume increases. This may produce elastic strain in the unit cell, which can inhibit oxygen vacancy diffusion due to the existence of lattice strain. If vacancy diffusion is inhibited, then contraction rate will be reduced.

It has been shown previously that contraction rate is a function of oxygen partial pressure, with \( \dot{\varepsilon} \) approximately proportional to \( P_{O_2}^{1/6} \) below \( P_{O_2}^{CRIT} \). If there is a direct relationship between lattice strain and contraction rate, then lattice strain should be a function of \( P_{O_2}^{1/6} \). The actual and 'expected' unit cell volumes, as shown in Figure 55, is replotted versus log \( P_{O_2} \) and is shown in Figure 56. The lattice strain, \( \Delta e_{lat} \), has been calculated as \( \left( \frac{\Delta V}{V_e} \right) \), where \( \Delta V \) is the difference between the measured volume and \( V_e \), where \( V_e \) is the expected volume. It was found that the only relationship between lattice strain and \( P_{O_2} \) that gives a slope of approximately 1/6 is a plot of \( \Delta e_{lat} \) versus log \( P_{O_2} \), Figure 57.

This implies that the following relationship between lattice strain and oxygen partial pressure is valid:

\[
\Delta e_{lat} = A + \frac{1}{6} \log P_{O_2} \tag{29}
\]

where \( A \) is a constant. This equation can be rearranged to give:

\[
A_1 e^{\Delta e_{lat}} = P_{O_2}^{1/6} \tag{30}
\]

where \( A_1 \) is a constant.

If this relationship is valid, then it can be seen that contraction rate, which is proportional to \( P_{O_2}^{1/6} \), should be proportional to \( e^{\Delta e_{lat}} \). Therefore, a plot of \( \ln \dot{\varepsilon} \) versus
Δε_{lat} should produce a straight line. This plot is shown in Figure 58, in which a linear relationship between ln ε and Δε_{lat} is evident. Therefore, an equation of the form below would satisfy this relationship:

$$\varepsilon \propto e^{\Delta \varepsilon_{lat}}$$ (31)

The oxygen content at which the deviation from linearity between unit cell volume and oxygen content occurs is close to the value of x in YBa$_2$Cu$_3$O$_x$ at which the contraction rate begins to decrease. This seems to support the hypothesis that lattice strain is inhibiting vacancy diffusion, thereby decreasing the contraction rate of YBa$_2$Cu$_3$O$_{7.8}$. Although the relationship between lattice strain and oxygen partial pressure as developed is empirical, it has been found to fit the data best. Thus, it is considered possible that the elastic strain induced within the lattice because of the removal of oxygen from the system may have something to do with the decrease in sintering rate for oxygen partial pressures below P$_{O_2}^{\text{CRT}}$. 
Figure 55. Unit cell volume as a function of oxygen content in YBa$_2$Cu$_3$O$_x$. The solid line indicates the expected volume.
Figure 56. Measured and expected unit cell volumes as a function of log $\text{PO}_2$. The difference in volumes is shown on the figure.
Figure 57. Lattice strain versus log \( \text{PO}_2 \), calculated from Figure 56.
Figure 58. Ln compaction rate versus lattice strain. A linear relationship is evident.
5 SUMMARY AND CONCLUSION

I) Isothermal sintering experiments were conducted to investigate the solid state sintering kinetics of YBa$_2$Cu$_3$O$_{7.5}$ over the temperature range 930 - 960°C and oxygen partial pressures from 0.001 to 1 atmospheres. The change in lattice parameters of YBa$_2$Cu$_3$O$_{7.5}$ over this oxygen partial pressure range was also studied in order to evaluate its effect on the sintering kinetics.

II) Two stages of contraction were evident during sintering of YBa$_2$Cu$_3$O$_{7.5}$ at all oxygen partial pressures. The first stage of contraction is rapid and nonlinear, while the second stage exhibits a steady state increase in contraction with time. During the first stage of contraction many concurrent processes may be occurring, which makes the analysis of this stage very complex. During the second stage of contraction only steady state sintering mechanisms are assumed to be operating. It is this region which is used for the analysis of sintering kinetics of YBa$_2$Cu$_3$O$_{7.5}$ with respect to temperature and oxygen partial pressure.

III) The sintering behavior of YBa$_2$Cu$_3$O$_{7.5}$ between 930 and 955°C is affected by oxygen partial pressure. It was found that contraction rate reached a maximum at some oxygen partial pressure, PO$_2^{\text{CRIT}}$, with decreasing contraction rates both above and below PO$_2^{\text{CRIT}}$. For PO$_2$ above PO$_2^{\text{CRIT}}$, contraction rate is proportional to PO$_2^{-1/6}$. For PO$_2$ below PO$_2^{\text{CRIT}}$, contraction rate appears to be proportional to PO$_2^{1/6}$. The sintering behavior of YBa$_2$Cu$_3$O$_{7.5}$ at 960°C is relatively independent of oxygen partial pressure, possibly due to the formation of a liquid phase at this temperature.

IV) The activation energy for sintering of YBa$_2$Cu$_3$O$_{7.5}$ for oxygen partial pressures above PO$_2^{\text{CRIT}}$ was determined by two separate methods of analysis. An activation energy of 176±12 kJ/mole was obtained from the effect of temperature on contraction rate. The
analytical method employed by Johnson and Cutler was also used, and an activation energy of 191±10 kJ/mole was obtained. For oxygen partial pressures below $P_{O_2}^{\text{CRIT}}$, an activation energy of 130±10 kJ/mole was obtained.

V) The unit cell volume and a-lattice parameter of YBa$_2$Cu$_3$O$_{7.8}$ decreased with decreasing oxygen partial pressure, while the c-lattice parameter increased. It was found that the unit cell volume did not decrease linearly with oxygen partial pressure.

VI) The sintering of YBa$_2$Cu$_3$O$_{7.8}$ at oxygen partial pressures above $P_{O_2}^{\text{CRIT}}$ can be attributed to an oxygen diffusion mechanism. The activation energies obtained for the sintering of YBa$_2$Cu$_3$O$_{7.8}$ are in good agreement with the activation energies reported for oxygen diffusion in YBa$_2$Cu$_3$O$_{7.8}$, supporting this mechanism.

VII) Several factors which may explain the sintering behavior of YBa$_2$Cu$_3$O$_{7.8}$ at oxygen partial pressures below $P_{O_2}^{\text{CRIT}}$ were developed. These relate contraction rate to copper vacancy diffusion, positive hole creation and lattice strain. However, Cu$^{3+}$ ions in the lattice are required for the formation of copper vacancies and positive holes. The presence of these ions in YBa$_2$Cu$_3$O$_{7.8}$ at the temperatures and oxygen partial pressures used in this study is unlikely. To relate contraction rate to lattice strain, an empirical equation satisfying the relationship $\dot{\varepsilon} \propto e^{\Delta e_{\text{lat}}}$, where $\Delta e_{\text{lat}}$ is the lattice strain, was developed. The significance of this relationship could not be established at the present time.
6 RECOMMENDED WORK

I) It has been observed that there was a maximum isothermal contraction rate of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \) at a \( \text{PO}_2 \text{CRIT} \). It would be interesting to determine if sintering samples for long periods of time at this oxygen partial pressures would produce full density materials, which are critically required for the commercialization of this compound.

II) It was also found that a certain period of time was required during the sintering of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \) before steady state conditions were reached. Part of this was attributed to structural equilibration of the contraction sample to the furnace environment. The time required for structural equilibration of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \) with respect to temperature and oxygen partial pressure could be more accurately determined by high temperature x-ray diffraction experiments and/or static experiments.

III) Yoo\(^{31}\) investigated the effects of oxygen partial pressure on the thermoelectric power of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \). A similar study could be carried out investigating the electrical conductivity of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \), as a function of temperature and oxygen partial pressure. This will confirm if the maximum in contraction rate is associated with a higher electrical conductivity.

IV) The present study was confined to investigating the sintering kinetics of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \) at and below oxygen partial pressures of 1 atmosphere. It would be worth investigating if the sintering kinetics of \( \text{YBa}_2\text{Cu}_3\text{O}_7.8 \) would change over a wider oxygen partial range.

V) A similar study on the effects of oxygen partial pressure on the sintering kinetics of other ceramic superconductors (eg. \( \text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \), \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \), etc.) should be carried out.
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Appendix I

Table I-1: Contraction Rate versus Oxygen Partial Pressure, 930°C.

<table>
<thead>
<tr>
<th>PO₂ (atmospheres)</th>
<th>Contraction Rate (ex 10⁵)</th>
<th>Log (PO₂)</th>
<th>Log (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3729</td>
<td>2.5431</td>
<td>-0.4285</td>
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Figure I-1. Contraction plots for YBa$_2$Cu$_3$O$_{7-\delta}$ at 930°C for the oxygen partial pressures indicated.
Figure 1-2. Contraction plots for YBa$_2$Cu$_3$O$_{7.8}$ at 930°C for the oxygen partial pressures indicated.
Table I-2: Contraction Rate versus Oxygen Partial Pressure, 945°C.

<table>
<thead>
<tr>
<th>PO₂ (atmospheres)</th>
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<th>Log (PO₂)</th>
<th>Log (e)</th>
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Figure I-3. Contraction plots for YBa$_2$Cu$_3$O$_{7.8}$ at 945°C for the oxygen partial pressures indicated.
Figure I-4. Contraction plots for YBa$_2$Cu$_3$O$_{7.8}$ at 945°C for the oxygen partial pressures indicated.
Table I-3: Contraction Rate versus Oxygen Partial Pressure, 955°C.

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<th>Log ((\dot{e}))</th>
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Figure I-5. Contraction plots for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 955°C for the oxygen partial pressures indicated.
Figure I-6. Contraction plots for YBa$_2$Cu$_3$O$_{7.5}$ at 955°C for the oxygen partial pressures indicated.
Table I-4: Contraction Rate versus Oxygen Partial Pressure, 960°C.

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<th>Log (é)</th>
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Figure I-7. Contraction plots for YBa$_2$Cu$_3$O$_{7.8}$ at 960°C for the oxygen partial pressures indicated.
### Appendix II

Table II-1: X-ray Powder Data for YBa$_2$Cu$_3$O$_6$

\[ a=3.852 \, \text{Å} \quad c=11.730 \, \text{Å} \quad P4/mmm \]

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<th>$I/I_0$ obs</th>
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Appendix III

Table III-1: Lattice Parameters of YBa$_2$Cu$_3$O$_{7-\delta}$ versus Oxygen Partial Pressure at 945°C.

<table>
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<th>c (Å)</th>
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