CHAPTER 5
HIGH TEMPERATURE RESISTIVITY STUDIES IN 
NON-STOICHIOMETRIC \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x} \)

The preparation of a non-stoichiometric \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x} \) from a fully oxygenated sample by a heat treatment using a given temperature profile and in continuously flowing helium atmosphere was carried out. The final oxygen concentration \( x \) was found to be dependent on the soaking temperature \( (T_A) \) during the heat treatment. The sample resistance was measured during the entire temperature profile using a four probe method. The resistivity results so obtained are analysed taking into consideration the present understanding of this class of materials.

5.1 INTRODUCTION

The superconducting material, \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x} \) (YBCO) is known to show variable oxygen concentration 'x'. It is well known that this variation in x is determined entirely by the oxygen content in its basal plane [Cava et al., 1987]. It is also well known that the variation in x is mainly responsible for many of its interesting physical properties [Jorgensen et al., 1987; Alario-Franco et al., 1987 and 1988]. Although at low temperatures (in the vicinity of the superconducting transition temperature \( T_c \)) the electrical resistance behavior of the material has been fairly thoroughly investigated [Tu, K.N., et al., 1987a; Park, S.I., et al., 1988; Tu, K.N., et al., 1988; Tu, K.N., et al., 1989; Ottaviani, G., et al., 1989; LaGraff, J.R., 1990; LaGraff, J.R., 1991; LaGraff, J.R., 1993a; LaGraff, J.R., 1993b; Ram, S., et al., 1992], there are not many reports of these measurements at relatively high temperatures. A change of the superconducting transition temperature \( T_c \) was observed when \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x} \) sample is heated from \( T_c \),
to room temperature [Jorgensen, J.D., et al., 1990]. There are reports on the high temperature resistance studies [Affronte, M., et al., 1996] on $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$, with $x < 0.5$, showing that the long relaxation times observed in resistivity measurements are related to order (or disorder) of oxygen defects. Photo-induced changes on the electronic properties of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.4}$ have been observed as well [Nieva, G., et al., 1992; Kawamomoto, K., et al., 1994; Tanabe, K., et al., 1994]. Theoretical studies [Semenovskaya, S., et al., 1992] have recently pointed out that a large variety of metastable phases can be formed with different local oxygen ordering. These authors find an intimate relationship between the oxygen ordering and the electronic properties of the non-stoichiometric YBCO [also Aligia, A.A., et al., 1994]. A wide region of the YBCO phase diagram is still experimentally unexplored. It has also been pointed out that very little work has been done in order to see whether time-dependent phenomena occur at high temperatures, i.e., in the phase diagram region that is the most favorable for the formation of the metastable phases.

It is all the more interesting to measure the electrical resistivity of the material at those temperatures where the resistance of the material carries the signatures of the phase formation at appropriate temperatures. At these temperatures the basal plane oxygen atoms undergo ordering / disordering transformations in addition to phase formation depending upon the thermal kinetics and the sample environment. A detailed description of the experiments carried out is given below.

### 5.2 HIGH TEMPERATURE RESISTIVITY EXPERIMENTS

A well sintered and fully oxygenated sample pellet, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ ($x \sim 0.9$), of typical dimensions 10 mm diameter and 1.0 mm thick was loaded in the high temperature resistivity measurement apparatus (HTRMA) [Narasimha Rao, G.V., et al., 1996 a]. The
details of this set up were discussed earlier in Chapter 3. The entire apparatus including the quartz tube was evacuated using a diffusion pump thoroughly 5 to 6 times and flushed with pure helium gas to remove traces of oxygen present in the quartz tube, before starting the high temperature resistance measurement experiment. During the entire experiment the sample was kept under continuous flow of helium gas. The flow rate of helium was maintained at about 2 - 3 bubbles per second as seen from a bubbler.

The soaking temperatures (T\textsubscript{A}) chosen were 350\(^\circ\)C, 385\(^\circ\)C, 435\(^\circ\)C, 455\(^\circ\)C, 485\(^\circ\)C and 525\(^\circ\)C. A dc constant current of 2, 5, 10 mA (using a Time Electronics current source model 9818) was passed through the outer probes in contact with the sample. The voltage across sample from the two inner probes was measured (using a 0.1 \(\mu\)volt resolution, HP Model 34410A microvolt meter). The sample heating was carried out in a flowing helium atmosphere using a temperature profile which is discussed below. Several experimental parameters including the current passed through the sample, the voltage measured across the sample, the sample temperature, the clock time etc., were recorded using an IBM compatible personal computer at intervals of 5 minutes throughout the duration of the temperature profile.
5.3 THE TEMPERATURE PROFILE USED FOR THE MEASUREMENT

The heat treatment for the sample consists of heating the sample from room temperature to a desired soaking temperature $T_A$ at 50°C per hour, soaking at $T_A$ for 24 hours and finally slow cooling to room temperature at 13°C per hour. The entire heat treatment of the sample was carried out in flowing helium gas atmosphere. A flow chart of sample heat treatment is shown schematically in the above chart. The Figure 5.1 shows the sample heat treatment versus experiment time.
5.3.1 REASONS FOR CHOOSING THIS TEMPERATURE PROFILE FOR THE SAMPLE

According to this temperature profile the sample pellet is heated in the first stage at the rate of 50°C. per hour to the desired temperature $T_A$. As has already been pointed out, at the temperatures of our interest (in the region of about 600°C) all the oxygen related activity of $Y_1Ba_2Cu_3O_{6+\delta}$ is confined to the oxygen atoms in the basal plane. Hence it is these oxygen atoms which become mobile due to the increased thermal energy and move around in the sample. Some reach the sample surface, get dislodged from the sample, and are mopped up by the flowing helium gas. The sample thus becomes oxygen deficient and non-stoichiometric. It is expected that soaking at $T_A$ for a period as long as 24 hours is adequate for the sample to reach an internal equilibrium.
with respect to the oxygen concentration x. To each $T_a$ there corresponds a particular value of the equilibrium oxygen concentration. It will be shown that these suppositions are borne out by the high temperature resistivity data. During the cooling stage the mobility of oxygen atoms again reduces and the final basal plane configuration corresponds to some temperature below $T_a$. It will be seen that the high temperature resistivity data gives some hints about this.

5.4 THERMOGRAVIMETRY STUDIES ON YBCO.

The thermogravimetric analysis (TGA) was done on a fully oxygenated YBCO sample with $T_A$ of 433°C, adopting the same temperature profile in helium atmosphere. It is noticed from the TGA curve that the loss of sample weight during heating stage was marginal up to about 320°C. Thereafter there was a rather abrupt loss of weight of the sample, which continued till about 8 hours of the start of the soaking stage. Then on, there was no significant change in the weight of the sample till the end of the experiment. Figure 5.2 shows the results obtained from the TGA experiment. This figure also contains the sample temperature profile and resistivity curve for a run with $T_A = 435°C$. Along the curve of the TGA data, a few positions are marked (a, b, c, and d) where the sample weights are marked more precisely. It is noticed from figure 5.2, that during cooling stage, the resistance of the YBCO sample has shown a deviation from the normal fall around 39 hours of the experiment time, while the TGA curve did not indicate any such signature at this time. This point is discussed in detail later in this chapter.
5.5 RESISTANCE BEHAVIOR OF YBCO SAMPLES AT HIGH TEMPERATURES.

Figures 5.3 and 5.4 show the resistance behavior of the \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x} \) sample during the temperature profile used with \( T_A = 385, 435 \) and \( 455^\circ\text{C} \). In figure 5.3 the sample resistance is plotted against the experiment time (in hours) and in figure 5.4 it is plotted against the sample temperature (\(^\circ\text{C}\)). The changes in resistivity of the sample during the entire temperature profile were found to be sensitively related to the soaking temperature \( T_A \), especially the resistance behavior during the cooling stage. These details are discussed at length below.
During the heating stage, it was expected that the oxygen would be continuously lost from the sample forming an oxygen deficient material depending upon the temperature $T_A$. The resistance showed a marginal increase, up to about 320 - 330°C. This could be attributed to some loss of oxygen present in the basal plane of the sample to the surroundings. This is also in conformity with the TGA experiment, indicating that there was a small decrease in sample weight up to this temperature. Above this temperature the TGA experiments showed a greater loss of sample weight extending to about 8 hours of soaking period and after that the sample weight remained more or less constant till the end of the experiment.
Coming back to the HTR experiment, the resistance of the sample above 320 to 330°C showed a steep increase. This steep rise in resistance continued till about 8 hours of the soaking stage, after that the resistance of the sample showed a tapering off behavior with time (It may be noted that the temperature was constant during the soaking stage). The further change in resistance without any loss of oxygen in the soaking stage could hence be attributed mainly to the redistribution of oxygen atoms within the grains. The results obtained from the high temperature X-ray diffraction experiments discussed in Chapter 6 also support this evidence. By the end of the soaking stage, the resistance of the sample showed a tendency to saturation, indicating the attainment of a state of an internal equilibrium with respect to oxygen distribution in the sample. The resistance behavior during the soaking stage could be fitted to a single exponential function with a characteristic relaxation time $\tau$. The function used was
\[ Y = A_0 \left( 1 - \exp \left( -t / \tau \right) \right) + A_1 \]

A typical graph of the fitted relaxation function over the resistance data during the soaking stage is shown in figure 5.5. The figure of merit obtained was very high for the fit of the experimental data with the relaxation function shown above, indicating that the relaxation time \( \tau \) obtained in this way is highly reliable, and can be used for drawing inferences about the underlying mechanisms.

![Resistance Behavior - Soaking Stage](image)

**Figure 5.5:** Resistance behavior of YBCO sample during soaking stage, fitted to a relaxation function.

The relaxation time \( \tau \), obtained from the best fits for the soaking temperatures \( T_A = 385, 435, 455, 483 \)°C, are tabulated in table 5.1.
Table 5.1: Soaking temperature \( (T_A) \) and relaxation time \( \tau \) data.

\( \tau \) shows an Arrhenius behavior with the temperature from which an activation energy of 0.7 eV was extracted. The Arrhenius plot is shown in Figure 5.6 for \( T_A = 385, 435, 455, \) and \( 483°C \). Samples.

The measured activation energy compares very well with tracer diffusion data [Rothman, S. J., et al., 1989]. From the known diffusion constant, using the value of \( \tau \) obtained from our studies, it can be inferred that the diffusion length involved is about 14 micrometers, which is typically the grain size in our samples. Hence it is inferred that the process involved here is the self diffusion of oxygen within the grain.
After the completion of the soaking period, the sample temperature was slowly lowered at 13° per hour to room temperature. The resistance curve during this stage showed some interesting features. Initially all the samples showed metallic behavior. The resistance continued to fall linearly with the temperature up to a temperature $T_1$ which depends on the stoichiometry $x$ at the end of the soaking period, where a change in the slope occurred. This feature was predominantly seen for the samples with low $x$ values. This was followed by a further linear fall of the resistance with temperature. It is tempting to connect up the $T_1$ values in this study to the temperatures $T^*$ associated with the formation of the pseudogap in the charge carrier excitation spectrum in underdoped superconductors [Batlogg, B., et al., 1994] which is discussed in detail in Chapter 1.
According to another point of view, the deviation of resistance from linearity could be attributed to the rearrangement or ordering mechanism of the oxygen atoms in the basal plane, taking place in the oxygen non-stoichiometric sample. If that is so, the minima in the derivative plot of resistance data during cooling stage should correspond to the temperature $T_{\text{min}}$, where the oxygen non-stoichiometric sample obtained by initially soaking at temperature $T_A$, should be soaked once again for long periods for producing a highly ordered material on a macroscopic scale. Figure 5.7. shows the derivative plot for the samples corresponding to the $T_A's = 385, 435, 455^\circ\text{C}$. The TGA and HTXRD curves during cooling stage did not show any special features at the temperatures where changes in slope have occurred in the high temperature resistivity graphs, especially in $435^\circ\text{C}$. case. This indicates that the non-linear fall of resistance during cooling stage is not associated with any structural change. Comparison with TGA shows that there is also no concomitant change in sample weight. Therefore it is highly plausible that the anomalous resistance behaviour at $T_1$ is related to the pseudogap temperature ($T^*$) discussed in Chapter 1.
In another experiment (Figure 5.8) the sample was soaked for a second time for another 48 hours at 245°C during cooling stage. During the second soaking stage the resistance of the sample remained constant throughout the second soaking stage. This indicates that the resistance characteristics of the sample did not get modified even after 48 hours of soaking at 245°C. This also confirms that the electrical probes are faithfully tracking the resistance of the sample and the changes of resistance shown in the other experiments are genuine features of the sample.
It is noticed that in all the cases the electrical contacts were found broken below about 180°C during the cooling stage. This has resulted in an open circuit for resistivity measurements. This is probably due to the formation of an insulating layer on the sample surface resulting in an increased contact resistance between the current probes and the sample. The maximum permissible overall current circuit resistance is determined by the compliance of the constant current source which was 12 V in the present case.
5.6 OTHER STUDIES CARRIED OUT ON THE SAMPLES AFTER COMPLETION OF HTR RUNS.

All the samples at the end of the resistivity runs were analysed for phase identification by XRD studies and for superconducting properties by ac susceptibility measurements. The XRD patterns show the presence of mixed phase for all the end samples even for the small values of $x$. Rietveld refinement calculations show the presence of both orthorhombic and tetragonal phases in all the cases. The volume fraction of the orthorhombic component, as obtained from the Rietveld refinement analysis, is less for the samples with higher soaking temperature, $T_A$.

Figure 5.9 shows the Rietveld refinement carried out on the XRD data corresponding to the sample with $T_A = 435^\circ$C. From the figure 5.9, it is clear that there exists a two phase mixture corresponding to ortho and tetra fractions in the end sample.
Figure 5.9 X-ray Rietveld plot of $Y_1Ba_2Cu_3O_{6.6}$ sample ($TA = 435^\circ C$.)
Table 5.2: Rietveld refinement results of YBCO samples

The ac susceptibility data for the high temperature resistivity end samples corresponding to the $T_A = 385$, $435$ and $455^\circ$C, are shown in figure 5.10. It is evident that the samples with $T_A = 385$, $435$ and $455^\circ$C, are all superconducting, the superconducting transition temperatures ($T_c$) varies according to the soaking temperature $T_A$. The transitions were broad and the signals were relatively weak.

<table>
<thead>
<tr>
<th>Soaking Temp. (°C)</th>
<th>385</th>
<th>435</th>
<th>455</th>
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<tr>
<td>O$_7$ Phase (Mass %)</td>
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<td>84.45</td>
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<tr>
<td>O$_6$ Phase (Mass %)</td>
<td>0.21</td>
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<td>39.66</td>
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<td>Fig. Merit (S)</td>
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<td>1.99</td>
</tr>
<tr>
<td>a lat. (Tetra)</td>
<td>3.8719</td>
<td>3.855</td>
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<tr>
<td>c lat. (Tetra)</td>
<td>11.2168</td>
<td>11.759</td>
<td>11.7638</td>
</tr>
<tr>
<td>density (Tetra)</td>
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<td>6.1658</td>
</tr>
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</tr>
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<td>3.8726</td>
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</tr>
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<td>$T_c$ end (95%)</td>
<td>36.12</td>
<td>5.04</td>
<td>4.90</td>
</tr>
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</table>
5.7 SUMMARY AND CONCLUSIONS

The high temperature resistance studies in helium atmosphere were carried out on oxygen non-stoichiometric YBCO pellets which were fully oxygenated earlier. The temperature profile used produces the oxygen non-stoichiometry in the compound, the resistance behaviour of which is probed and the results thus obtained are discussed. The oxygen non-stoichiometry, $x$ in $\text{YBa}_2\text{Cu}_2\text{O}_{6-x}$ is dependent on the soaking temperature $T_a$. The resistance increase of the sample below 320°C is attributed to partial loss of oxygen. A steep increase in resistance of the sample was observed from about 320°C during heating stage to about 8 hours of the initial soaking stage. This large increase in resistance of the sample is understood taking into consideration the results from TGA data which indicates gross loss of weight of the sample owing to oxygen loss from the sample. The HTXRD runs discussed in Chapter 6 also shows gross changes occurring in the sample during this stage, indicating the sample losing oxygen on a rapid scale.
resulting from a relatively more oxygenated orthorhombic system to a less oxygenated orthorhombic system with simultaneous building up of a tetragonal phase. The increase in resistance from the start of the soaking stage, till the completion of the soaking stage is fitted to a single exponential process and the relaxation time, \( \tau \) was extracted. The \( \tau \) showed an Arrhenius behavior with the temperature from which activation energy for the process was extracted. This activation energy was found to be 0.7eV. The measured activation energy compares very well with the tracer diffusion data available in the literature. From the known diffusion constant, using this value of \( \tau \) obtained in these studies, it was inferred that the diffusion length involved is about 14 micrometers, which is typically the grain size [Rothman, S.J., et al., 1989] of these samples. The resistance data in the cooling stage showed a metallic behavior upto a temperature \( T_1 \) which depends on \( x \), where a change in slope occurs, seen prominently for low \( x \) values. This was followed by a further fall in the resistance with temperature. The \( T_1 \) value in this study correspond to the temperature \( T^* \) associated with the formation of pseudogap in the charge carrier excitation spectrum in underdoped superconductors, known from other studies in the literature.
5.8 REFERENCES


