CHAPTER 11

SYNTHESIS AND CHARACTERIZATION OF HIGH TEMPERATURE SUPERCONDUCTOR, YBa$_2$Cu$_3$O$_7$

1.1 Introduction

This chapter, not directly connected with the previous chapters, is in tune and conformity with the CSIR project executed during the extended period, as clarified in the preface of this thesis.

Superconductivity is the phenomenon in which the resistivity of a metallic conductor falls abruptly to
zero at some temperature, above the absolute zero, called the critical or transition temperature $T_c$. The normal-to-superconductor transition is perfectly reversible with no hysteresis and is an example of a second order phase transition. In addition to zero electrical resistance below $T_c$, a superconductor exhibits "Meissner effect" according to which a superconductor at low applied magnetic fields becomes perfectly diamagnetic and thus expels magnetic flux from within.

A large number and a wide variety of pure metals, alloys, intermetallics, binary compounds and ternary compounds containing oxygen, sulphur, selenium, phosphorous, etc. are known to exhibit superconductivity at low temperatures (Liquid helium, 4.2 K). The search for high temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed matter physicists and material scientists. To obtain superconducting state reaching beyond the technological temperature barrier of 77 K, the liquid nitrogen boiling point, could be one of the greatest triumphs of scientific endeavour of this kind. Inspite of the great efforts over the past 80 years, since the discovery of the phenomenon, the superconducting transition temperature $T_c$ remained until
1986 below 23.2 K, the $T_c$ of Nb<sub>3</sub>Ge first discovered by Valencia et al. [223]. In face of this gross failure to raise the transition temperature, new approaches [224-226], taking advantage of the possible strong non-conventional superconducting mechanisms, have been proposed and tried [227-231]. In April 1986, the situation changed drastically when Bednorz and Muller [232] reported the possible existence of percolative superconductivity in $(\text{La}_{1-x}\text{Ba}_x)\text{Cu}_3\text{O}_7-y$ with $x = 0.2$ and 0.15 in the 30 K range. The literature survey uptodate reveals that the high temperature superconductivity above 77 K occurs only in compound systems consisting of a phase or phases in addition to or other than $\text{K}_2\text{N}_2\text{F}_4$ phase in RACO systems, with $R = \text{La}$ or Y and $A = \text{Ba}$ or Sr. It may be pointed out that the lattice parameters, the valence ratio, and the sample treatments, all play a crucial role in achieving superconductivity above 77 K. The role of different phases present in superconducting structure is a matter of controversy. Extensive studies in this direction have been conducted and a rapid advance has occurred culminating in the reports by Wu et al. [233] and Hor et al. [234] of an onset temperature greater than 90 K in Y-Ba-Cu-O compounds. Tse et al. [236] recently discovered $\text{YBa}_2(\text{Cu}_{3-x}\text{Ag}_x)\text{O}_{7-y}$ compound in which they observed onset
transition temperature around 260 K for $x = 1$. In the present investigation, fundamental studies on $YBa_2Cu_3O_7$, in the form of polycrystalline pellets, have been undertaken at an ambient pressure.

11.2 Structural features of $YBa_2Cu_3O_7$

The essential features of $YBa_2Cu_3O_7$ are [236, 237].

1. It is an oxygen deficient, orthorhombically distorted perovskite with unit cell dimensions $a = 3.882 \text{ Å}$, $b = 3.891 \text{ Å}$ and $c = 11.677 \text{ Å}$.

2. $Y^{3+}$ and $Ba^{2+}$ ions have 8-fold and 10-fold oxygen co-ordinations respectively, whereas copper exists in $2^+$ and $3^+$ states (or $Cu^{2+}$ and $O^{1-}$) (see figure 11.1).

3. In $YBa_2Cu_2Cu^{3+}O_7$ two kinds of Cu atoms exists in the structure ($2 Cu^{2+}$ and $C^{1+}$ ions).

4. $T_C$ is highly sensitive to oxygen stoichiometry in $YBa_2Cu_3O_7-\delta$ and is exhibited only for $0.05-0.2$. Then $T_C$ decreases to 60 K for $\delta = 0.20 -0.40$; whereafter $\delta \geq 0.5$, the compound becomes insulating.
The structure permits extensive chemical substitution at the Y, Ba, Cu and perhaps at the 'O' sites as well. Due to the Cu-O planes and chains, anisotropy in physical properties are exhibited, excepting $T_c$.

### 11.3 Synthesis

The ceramic oxide superconductor, YBa$_2$Cu$_3$O$_7$, has been prepared by the direct solid state reaction from the high purity metal oxides and carbonates, following the reaction:

\[ Y_2O_3 + 2BaCO_3 + 3CuO \rightarrow YBa_2Cu_3O_7 + 2CO_2 \]

1. Appropriate quantities of the reactants, $Y_2O_3$ ($225.87 / 2 = 1.129 \text{ g}$), $BaCO_3$ ($2 \times 197.35 = 3.9470 \text{ g}$) and $CuO$ ($3 \times 79.54 = 2.3862 \text{ g}$) were (a) weighed accurately on a metlar balance and thoroughly ground with acetone for 30 min in an Agate Mortar, (b) dried in air, and (c) heated at 940°C in a platinum crucible for 24 hrs.
2. After air-quenching, the material was ground for 5 min and heated at 940°C for 24 hrs.

3. It was again ground and heated once more at 940°C for 24 hrs.

4. The black powder so obtained was pressed into a pellet, 8 mm in diameter and 2 mm thick.

5. The pressed pellets were then heated at 950°C for 24 hrs and then cooled. The pellets were black in colour.

6. In order to ensure that the oxygen content in the resulting YBa$_2$Cu$_3$O$_{7-\delta}$ (\(\delta = 0.05 - 0.70\)) is optimised, the pellets are annealed in flowing oxygen gas in a tubular furnace at 900°C for 24 hrs, then at 600°C for 24 hrs and then slowly cooled down to 200°C. Thereafter the furnace is switched off, continuing the flow of oxygen for a few hours. The pellets are still black in colour and are now well-sintered. They are ready for characterization as described in the following section.
11.4 Characterization

11.4.1 X-ray diffraction

The pellet of YBa$_2$Cu$_3$O$_{7-\delta}$ was broken into small pieces, then ground well and X-ray diffraction pattern was taken using CuK$_\alpha$ radiation. From the XRD pattern (figure 11.2), d values were calculated using the relation $2d \sin \theta = n\lambda$. These 'd' values (Table 11.1) are in good agreement with the standard data [238] and it shows the orthorhombic phase.

11.4.2 Analysis for oxygen

By the standard method reported [239] in the literature, the oxygen in YBa$_2$Cu$_3$O$_{7-\delta}$ is then determined as follows:

The experiment is carried out in two parts

(1) Experiment A

About 25 mg of the powder is taken in an iodide flask, to which is added 7 ml of 1 M KI. To this 7 ml of 0.7 M HCl is added. The whole is shaken well till all the powder dissolves and then titrated against 0.01 M thiosulphate solution from the burette. When the colour
Table 11.1

'd' values obtained from X-ray powder diffractogram of $YBa_2Cu_3O_7$ (λ = 1.542 Å)

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<th>Sl. No.</th>
<th>2θ</th>
<th>θ</th>
<th>d = $\frac{nλ}{2 \sin θ}$</th>
<th>d ASTM</th>
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**Table 11.1 (cond.)**
Fig. 11.1

Structural features of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \)
Fig. 11.2

X-ray powder diffractogram of YBa$_2$Cu$_3$O$_7$
Fig. 11.3

Four probe schematic arrangement.
Fig. 11.4

Variation of resistivity with temperature.
of the solution changes to pale yellow, 2 ml of 1% starch solution is added and titrated with thiosulphate solution. End point is the sudden colour change from dark blue to colourless solution. Let the volume of the thiosulphate be $l_1$ ml.

(2) **Experiment B**

About 30 mg of the powder dissolved in 10 ml 1 M HCl is boiled for 10 minutes and cooled to room temperature. Then 10 ml of 0.7 M KI is added and titrated against thiosulphate solution. Let the volume of thiosulphate be $l_2$ ml.

$$A = \frac{l_1}{x} \quad \text{and}$$

$$B = \frac{l_2}{y} \quad (11.1)$$

where $x$ and $y$ are the weights of the sample taken for the experiments A and B respectively.

**Case (i)**

If $A > B$

$$\frac{A - B}{B} \times 3 = Z = \text{Total amount of } Cu^{3+} \text{ in 1 2 3} \quad (11.2)$$
Total number of Cu in 1 2 3 = 3

Total amount of Cu\(^{2+}\) ion in 1 2 3 = (3-Z) (11.3)

In YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) for charge neutrality

\[(+3) + (2 \cdot +2) + (Z \cdot +3) + (3-Z) \cdot +2 + 2(7 - \delta) = 0\]

\[
7 - \delta = \frac{7 + (Z + 3) + (3-Z)}{2}
\]

or

\[
7 - \delta = \frac{13 + Z}{2}
\]

\[
\delta = \frac{1 - Z}{2} \quad (11.4)
\]

Case (ii)

If \(A < B\)

\[
\frac{B-A}{A} \times 3 = Z' = \text{Total amount of Cu}^+ \text{ ion in 1 2 3} \quad (11.5)
\]

Total amount of Cu\(^{2+}\) in 1 2 3 = (3 - Z') (11.6)

\[
7 - \delta = 7 \cdot (Z' + 1) + (3 - Z') \cdot +2
\]

or,

\[
7 - \delta = \frac{13 - Z'}{2}
\]

\[
\delta = \frac{1 + Z'}{2} \quad (11.7)
\]
In the present case,

\[ A = \frac{14 + 2}{25} = 0.568 \]

\[ B = \frac{12 - 8}{30} = 0.427 \]

\[ \frac{A-B}{B} = 0.330 \]

\[ Z = \frac{A-B}{B} \times 3 = 0.990632 \]

\[ \delta = \frac{1 - Z}{2} = 0.004684 \]

11.4.3 Test for superconductivity

The 'Van der Pauw' method was employed for the measurement of the four probe electrical resistivity. This is a very general method and places no restrictions on the size or shape of the sample. The conditions to be satisfied, however, are:

(i) the samples should be uniformly thick
(ii) the electrical contacts should be made near the periphery; and
(iii) the sample should not contain cracks or isolated holes.
The four lead wires were attached at arbitrary positions around the edge of the sample. A current, $I$ is passed through adjacent leads, e.g. A and B (figure 11.3) and the potential drop, $V$ across the other two leads, say C and D is measured. The apparent resistance, $R_1$ is thus calculated:

$$R_1 = \frac{V_{CD}}{I_{AB}} \quad (11.8)$$

An apparent resistance, $R_2$ is also then determined as,

$$R_2 = \frac{V_{BC}}{I_{AD}} \quad (11.9)$$

The resistivity, $\rho$ is related to $R_1$ and $R_2$ as

$$\exp \left( - \frac{\pi R_1 t}{\rho} \right) + \exp \left( - \frac{\pi R_2 t}{\rho} \right) - 1 = 0 \quad (11.10)$$

where $t$ is the thickness of the sample. For an anisotropic sample with four nearly rectangular contacts, with contact dimensions $l_1$ and $l_2$ and uniform thickness $l_3$, the specific resistivity in two perpendicular directions is given by

$$\rho_1 = H_1 E R_1 \quad (11.11)$$
where $E$ is the effective thickness and $H$ is a function dependent on the ratio $(l_2/l_1)$ for $\rho_1$ and $(l_1/l_2)$ for $\rho_2$. The specific resistance is calculated by measuring $R_1$ and $R_2$ which will give $l_1/l_2$ (which in turn gives $H$) and using the equation (11.11)

$$\rho(\text{ohm. cm}) = H E R_1 = H t R_1$$

where $t$ is the actual thickness of the specimen.

Indium metal contacts were made on the pellets and the copper lead wires attached. The pellet was then mounted over the Cu plate in a sample holder. The temperatures are measured using a calibrated Chromel - Alumel thermocouple kept near the sample. The entire setup for the low temperature measurement (300 - 10 K) using RMC liquid Helium cryostat.

Figure 11.4 represents the resistivity versus temperature data obtained of the YBa$_2$Cu$_3$O$_7$ sample. These results demonstrate unambiguously that the superconductivity occurs in YBaCO system with a transition
between 85 and 96 K. The observed sharp transition indicates that a homogeneous ceramic sample was obtained. After 96 K, the resistivity increases with temperature, when the material passes into the normal state.

11.5 Conclusions

The superconductivity transition temperature $T_C$ and $T_\text{on}$ of the prepared $\text{YBa}_2\text{Cu}_3\text{O}_7$ are 91 K and 85 K respectively. A sharp drop of resistivity of 96 K implies homogeneity of the material prepared. The results are an evidence of stable and reproducible high $T_C$ superconductivity at 91 K in the single phase compound, $\text{YBa}_2\text{Cu}_3\text{O}_7$. 