CHAPTER 2
PREPARATION AND CHARACTERIZATION OF YTTRIUM BARIUM COPPER OXIDE SAMPLES

In this chapter, details of the methods employed for the preparation of the superconductor material, \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}, \ 0 < x < 1 \), (YBCO) are discussed. These methods are (1) the solid state vacuum calcination method and (2) the citrate combustion route. Some of the parameters which influence the final quality of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x} \) are also discussed.

2.1 INTRODUCTION

In order to study the interesting properties of the oxygen non-stoichiometric \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}, \ 0 < x < 1 \), it was essential to prepare a phase pure material and oxygenate it, such that the \( x \) is close to 1. Most investigations of the YBCO compound, have been carried out on the materials prepared by reacting \( \text{Y}_2\text{O}_3 \), and \( \text{CuO} \) with \( \text{BaCO}_3 \) [Cava, R.J., et al. (1987), Rao, C.N.R., et al. (1987)]. In this method the stoichiometric quantities of high-purity materials are ground thoroughly and heated initially in the form of powder at around 950°C for 24 hours. Following the calcination step the powder is ground, pelletised and sintered at the same temperature for another 24 hours. Finally, the annealing is carried out in an oxygen atmosphere around 500°C for 24 hours to obtain the orthorhombic YBCO phase showing superconductivity at \( T_c \approx 90 \)K. The oxygen annealing is normally carried out below the orthorhombic - tetragonal transition temperature (~ 680°C); tetragonal \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x} \) (generally, \( 0.0 < x < 0.4 \)) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. In addition, the CO\(_2\) released from the decomposition
of BaCO₃ can react with YBa₂Cu₃O₆₋ₓ to form non-superconducting phases at the grain boundaries. One way of avoiding the evolution of CO₂ during the synthesis is to use BaO₂ instead of BaCO₃ [Leskela, M., et al., (1988); Rao, C.N.R., et al., (1988)]. Some impurities or side products, which are usually observed in the preparation of YBa₂Cu₃O₆₋ₓ are BaCuO₂, Y₂BaCuO₅, Y₂Cu₂O₅ etc. The ternary phase diagram in figure 2.1 illustrates the complexities of this cuprate system.

Gadalla et al., (1989) have reported from their DTA and TGA studies is the formation of 123 compound from 123 mixture which is a three step process involving the formation of 011 and 211 phases as intermediate phases. From TG/DTA studies, they have estimated overall activation energy for the formation of 123 compound to be 116 Kcal / mol. From the kinetics of 202, 011, 211 and 123 phase formation by diffusion-couple experiment [Floor, G., et al., 1990] the rate reaction constant k, has been estimated. These authors report that 123 compound formation from 202 and 011 phase is the fastest. The rate of formation of other phases in order of decreasing speed is 011, 211 and 202. Ruckenstein, E., et al., (1989), carried out kinetics of formation of 202, 011, 123 compounds by X-ray diffraction studies, using appropriate stoichiometric mix of oxide / carbonate precursors, calcined at 940°C. in air for different annealing time. Their conclusions match those of Floor, G., et al., (1990). There exist several other methods for preparation of YBCO powders. These include coprecipitation and precursor methods. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained when the following conditions are satisfied. (i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast. (ii) The solid precipitating out of the solution should be really insoluble in the mother liquor. The anions generally preferred for coprecipitation of
Figure 2.1 Ternary phase diagram of cuprate system in air.

The important chemical reactions taking place in the formation of $Y_1Ba_2Cu_3O_7$ from the reactants $Y_2O_3$, CuO, BaCO$_3$ are

\[
2BaCO_3 + \frac{1}{2}Y_2O_3 + 3CuO \rightarrow YBa_2Cu_3O_{6.5} + 2CO_2
\]

\[
YBa_2Cu_3O_{6.5} + \frac{1}{2}O_2 \rightarrow YBa_2Cu_3O_7
\]

**2.2 PREPARATION OF INITIAL POWDERS**

The preparation of the phase pure and fully oxygenated sample was done by employing two methods. These are (1) the citrate combustion route [Kakihana, M., et al., 1989], and (2) the solid state vacuum calcination method [Balachandran, U., et al., 1989]. Some of the important parameters which influence the quality of final $Y_1Ba_2Cu_3O_{6-x}$ are, the reaction temperature, soaking time during oxygenation and subsequent rate of cooling, effects of kinetic hindrance / impedance to the free
flow of oxygen during reaction and during oxygenation, impurity phase
(BaCuO₂, Y₂BaCuO₅) formation etc. and some of the methods to overcome these
problems are discussed in this chapter.

2.2.1 CITRATE COMBUSTION ROUTE.

There are a number of methods available in literature for preparation of YBCO
powder. Majority of the preparation of YBCO has been performed by usual ceramic
method [Chu, C.W., et al., 1987]. This dry powder mixing method, however, does not
allow for sufficient control of particle morphology and size to produce dense materials
with uniform distribution of the cations even after repeated mixing. However this can be
achieved by employing solution techniques [Barboux, P., et al., 1988]. On the other
al., 1988, Pankajavalli, R., et al., 1988] techniques to produce highly pure YBCO
superconductors based on citrate complexes uniformly dispersed into a mixed solvent of
ethyleneglycol and water as adopted by Masato Kakhana, et al., 1989, were shown to
produce good quality material. Among the methods of preparation of pure YBCO, the
citrate combustion route adopted by Kakhana, M., et al., 1988, was reported to be
showing a very sharp superconducting transition temperature at 91K with a width (10-
90%) of 0.6 K. Considering these points, it was decided to adopt this method for
preparation of YBCO samples. The only change made in the preparation process is using
BaCO₃ instead of BaO used by Kakhana. However, this method was subsequently
discarded due to the presence of impurity phases like BaCuO₂, Y₂BaCuO₅ etc., on a
large scale, in the powder samples. These impurity phases could not be removed even
during the sintering stage.

Requisite quantities of analytical reagent grade chemicals, Yttrium Oxide
(Y$_2$O$_3$, Indian Rare Earths Ltd., Alwaye, purity 99.99%), Barium Carbonate (Ba$_2$CO$_3$, E. Merck, Darmstadt, purity 99%) and Copper (II) Oxide (CuO, E. Merck, Darmstadt, purity 99%) were taken separately such that the final product, Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ with maximum $x \sim 1$ would be around 25 grams per batch. These chemicals were then transferred to an agate pestle and mortar and ground thoroughly. This powder was then transferred to a 500 ml beaker and small quantities of analytical reagent quality nitric acid was slowly added to it and warmed on a hot plate. Additional quantity of nitric acid was added till all the solid mass dissolved completely. This step was required to convert all the cations to corresponding cation nitrates [Kakihana, M., et al., 1989]. The beaker containing this solution was then placed on a hot plate in a fume hood. The solution was evaporated at low heat to make a powdery material with constant stirring. The NO$_2$ gas evolved during this process was quickly removed by the exhaust fan in the fume hood. These nitrates were then dissolved in water to make a solution and citric acid was added to this in the proportion of 1.9 grams to 1 gram of barium nitrate, Ba(NO$_3$)$_2$. This was followed by the addition of requisite quantity of ethyleneglycol, based on 10 ml of ethyleneglycol per 1 millimol of the yttrium present in the solution. The solution was then condensed at 120°C (to remove excess nitric acid) until a green-white colloidal precipitate was obtained. The residual solvent was evaporated at 200°C from the colloidal solution to obtain a brown black oily gel. This gel was subsequently decomposed to a solid by heating it on a hot plate. At this stage it was found to catch fire which resulted in brown-black powder. This brown-black powder is considered as the initial powder obtained from the citrate combustion method for heat treatment (described in section 2.3 below) for preparation of pure YBCO powder.
2.2.2 VACUUM CALCINATION METHOD.

The alternate method used for preparing the homogeneous mixture of precursors before calcining is the vacuum calcination method [Balachandran, U., et al., 1989]. The vacuum calcination method has certain advantages over the normal solid state reaction method. For example, the reduced pressure removes the CO$_2$ released during the reaction much more effectively before it has a chance to back-react with the YBCO, to form BaCO$_3$, Y$_2$O$_3$, CuO and Y$_2$BaCuO$_5$ depending on the temperature. The BaCO$_3$ decomposes in the proximity of Y$_2$O$_3$ and CuO at a relatively low temperature, viz. onsets at 620°C. The corresponding temperature is more than 800°C in ambient pressure synthesis [Raghunathan, V.S., et al., 1991] as known from TGA studies. Lower temperature calcination also results in the lower particle size (approximately 4µmeter). The resistivity of the so synthesised samples is typically 500 mΩcm at 300 K and the superconducting transition has a width of 3K (powder ac susceptibility).

Stoichiometric quantities of Y$_2$O$_3$, Ba$_2$CO$_3$ and CuO were taken separately such that the final product, Y$_{1-\delta}$Ba$_2$Cu$_{2-x}$O$_{6-x}$, with maximum x ~ 1 would be approximately 25 gram per batch. The weighed materials were then transferred to an agate pestle and mortar and ground thoroughly with HPLC grade butan-2-one (H$_2$O content < 0.05%) to make a slurry. The slurry was mixed thoroughly for about 2 hours and dried overnight under the infrared lamp. The resulting black mass was powderized again and loosely packed in a recrystallized alumina cylinder.

2.3 PRELIMINARY TREATMENTS AND SINTERING OF YBCO SAMPLES.

The as prepared powder precursors were given preliminary heat treatments to form the desired pure compound following the procedure discussed here. The powder
sample was transferred to a 40-mm diameter recrystallized Alumina cylinder with both ends open. One end of the cylinder was covered with a thin, well perforated silver metal foil for free passage of oxygen gas through the cylinder when sample powder is placed in it. Silver metal is known to be non reactive with the chemicals present in the cylinder during the entire process of heat treatment. In order to prevent fine powder spilling over through the pores of the silver metal foil a thin layer of glass wool with a backing of stainless steel wire gauge was placed behind the perforated portion of the silver foil. All these were tied together firmly to the recrystallized alumina cylinder with a stainless steel wire. A similar procedure was used on the other side of the cylinder after transferring the sample into it. This procedure was necessary to prevent fine powder material of the sample coming out of the recrystallized alumina cylinder, spreading all over the quartz tube when the quartz tube was evacuated using a rotary pump. The perforation in the silver foil is meant to allow free flow of oxygen over the sample. This cylinder was then placed at the middle of the hot zone in a 65-mm diameter 1500 mm long horizontal tubular furnace. Initially the quartz tube was evacuated to the best vacuum that a rotary pump could generate. Slowly the oxygen gas was let in. The flow of oxygen was regulated through the quartz tube such that the pressure inside the quartz tube was maintained at two millibar. This rate of flow of oxygen was continued till the completion of the first soaking stage of the temperature profile given below. A temperature profile for heat treatment of the sample was programmed in a PARTLOW MIC 6000 Model programmable temperature controller using the following flow chart.
The oxygen pressure inside the quartz tube near the sample was maintained at two millibar with dynamic rotary vacuum. Pure oxygen gas flow at the rate of two - three bubbles per second was let into the quartz tube at the end of the 850°C soaking stage, till the end of the run. In the heating process, the starting chemicals lose CO₂ and react with each other forming Barium, Copper and Yttrium complexes under the prevailing temperature and oxygen partial pressure conditions. During the cooling stage the complexes react with each other resulting in the formation of Y₁Ba₂Cu₃O₆₋ₓ. On slow cooling to 450°C at the rate of 13°C per hour, the oxygen gets into Y₁Ba₂Cu₃O₆₋ₓ lattice at rates depending on the temperature. A second soaking step at 450°C for another 24 hours is allowed for the maximum oxygenation of the sample and phase stabilisation. Finally the sample is cooled to room temperature at 13°C per hour.

The sample powder was pelletised into several 10-mm diameter, 1.0 - 1.5 mm thick pellets by applying a load of 5.5 metric tons for a minute in a hydraulic press. These pellets were placed in a recrystallized alumina boat and reintroduced at the centre of the heating zone in the horizontal tubular furnace. For sintering the sample pellets the following temperature profile was used.
2.4 SAMPLE CHARACTERIZATION AND IMPURITY PHASE IDENTIFICATION.

The sample powder was placed on a low back ground X-ray sample holder plate, (Si 911) as a thin layer and introduced in the sample position of the Siemens D 500 Model θ/2θ powder diffractometer and a digital data of the powder diffractogram was recorded using Copper Kα radiation. The XRD data of the sample was recorded in the range of 5 to 70°2θ in step scan mode at a step size of 0.05°2θ with a step time 5 seconds. The recorded XRD data was then carefully analysed for impurity phases.

It is observed that there are impurity phases (BaCuO₂ and Y₂BaCuO₃) present in as prepared samples of citrate route as well as vacuum calcination route. However, the impurity phase concentration in the sample prepared via vacuum calcination route was comparatively smaller. Therefore, the preparation of YBCO sample via citrate route precursor method was discarded as the presence of impurity phases in large quantities would make further studies difficult. However, it was decided that there is some procedural error in sample preparation. After making several changes in the procedures and observing for impurity phase concentration, it was found that the impurity phase formation was due to the improper sample packing procedure, which did not allow
proper flow of oxygen gas through the sample and the surface area of the sample exposed to oxygen gas was very small which ultimately resulted in impurity phase formation. This point is discussed in detail later in the next section.

Figure 2.2 is the XRD pattern of the YBCO sample powder prepared via citrate route after preliminary treatment as described in 2.2. On detailed analysis of this XRD pattern, it was found to contain large amounts of impurity phases like BaCuO$_2$ (ICDD pattern # 38-1402) and Y$_2$BaCuO$_5$ (ICDD pattern # 38-1434). These impurity peaks are marked in figures 2.2 and 2.3 (a = BaCuO$_2$ and b = Y$_2$BaCuO$_5$). As this sample was containing relatively large amounts of impurity phases this procedure for preparation of YBCO was discarded.

XRD pattern of the sample powder prepared via vacuum calcination route was recorded (figure 2.3). This pattern was found to contain impurity phases including BaCuO$_2$ and Y$_2$BaCuO$_5$, but the magnitude of impurity phase is smaller as compared to the citrate route. It is also thought that during sintering stage the impurity phase concentration may reduce. Hence this powder was pelletised into several pellets and was sintered as described earlier.

A small portion of the sintered pellet was broken and powdered thoroughly and its XRD pattern recorded. This XRD pattern also showed additional Bragg peaks corresponding to the impurity phases such as BaCuO$_2$ and Y$_2$BaCuO$_5$.

### 2.5 Over Coming the Impurity Phase Formation

At this stage a serious thought was given to the entire sample preparation conditions to improve the quality of the sample. It was thought that the impurity phase formation may be due to presence of insufficient oxygen during high
Figure 2.2 XRD pattern of YBCO powder prepared via citrate combustion route.
Figure 2.3 XRD pattern of YBCO powder prepared by vacuum calcination method.
temperature soaking at around 850°C and subsequent cooling stages. It was thought that maintaining 2 millibar dynamic pressures of rotary vacuum with simultaneous flow of oxygen gas was necessary for quick removal of CO₂ liberated in the sample heating and soaking process. It is experienced that, as soon as the soaking process was completed, there should be sufficient amount of oxygen available to the sample for formation of desired phase. Insufficient oxygen partial pressure would lead to the formation of impurity phases such as BaCuO₂ and Y₂BaCuO₅. Therefore, the sample powder is placed in an open boat to have large surface area of the sample to interact with flowing oxygen gas, instead of keeping it in a partially closed cylinder. To prevent sample spilling over when rotary vacuum pump is started due to the differential pressure, a precision needle valve was incorporated on the rotary vacuum pump side to have a very fine control during the evacuation of the quartz tube. This precision needle valve was opened very slowly after switching on the rotary vacuum pump so that the sample top layer was not disturbed.

An XRD pattern of the sample powder after incorporating above changes in the preliminary sample heat treatment procedure was recorded. An analysis of this pattern showed that the intensity of the impurity peaks significantly reduced and the intensity of the characteristic peaks of Y₁Ba₅Cu₆O₁₉, namely (013) and (103), (110) Bragg peaks were high (figure 2.4).

There was also a small component of BaCuO₂ peak whose intensity was about 2% of maximum intense Bragg peak in the XRD pattern. The proportion of Y₂BaCuO₅ was negligible. At this stage it was decided to proceed further for sintering as BaCuO₂ phase may reduce at the sintering stage. At the end of sintering step it was found that the
Figure 2.4 XRD pattern of YBCO powder after 1 sintering stage.
impurity phase $\text{BaCuO}_2$ was reduced to about 1%.

To further reduce the amount of $\text{BaCuO}_2$ phase, the sintered pellets were reintroduced in the recrystallized alumina boat for another sintering step. The temperature profile used in this step was similar to the first sintering except that an additional soaking stage at 600°C for another 24 hours was introduced. The samples which underwent a second sintering step were studied in detail by XRD method. It was found that the Bragg peak intensity of the impurity phase $\text{BaCuO}_2$ was much less than 1% of the most intense Bragg peak in the XRD pattern (figure 2.5). The figures of merit, $F$ and $M$, are generated by the least-squares refinement program [Appleman, D.E., and Evans, H.T.].

It is also observed that the splitting of the (013) and (103), (110) Bragg peaks have improved due to the optimum oxidation ($x \geq 0.9$) of the sample. The $T_c$ onset for this sample was found at 89K (figure 2.6). These pellets were used for high temperature X-ray diffraction studies and high temperature resistivity measurements, the details of which are covered in later Chapters.
Figure 2.5 XRD pattern of YBCO powder after additional annealing at 600°C.
These fully oxygenated $Y_1Ba_2Cu_3O_{6-x}$ sample pellets were used in the preparation and further studies like high temperature resistivity and high temperature X-ray diffraction studies of oxygen non-stoichiometric compounds by adopting a specific temperature profile described in Chapter 5. During the entire temperature profile the resistivity ($\rho$) of the sample and X-Ray Diffractogram (XRD) was monitored. The oxygen stoichiometry is found to depend upon the soaking temperature $T_A$. Samples with different oxygen content $x$ were synthesised by varying $T_A$. The thermogravimetric analysis (TGA) was done on a sample with $T_A$ of 433°C, adopting the same temperature profile in helium atmosphere (oxygen content $\leq$ 30 ppm). The superconducting transition temperature ($T_C$) was also measured on samples quenched from several selected times along the employed temperature profile. The samples
investigated had oxygen non-stoichiometry in the range of 6.7 to 6.28. The $Y_1Ba_2Cu_3O_{6.28}$ sample recorded a $T_c$ of 9K, the lowest measured so far. The experiments carried out on these non-stoichiometric compounds are discussed in later chapters.

2.6 SUMMARY AND CONCLUSIONS

The preparation of initial powders of yttrium barium copper oxide were done by two methods (1) Citrate precursor route and (2) Vacuum calcination method. It was observed that in both cases the impurity phases such as BaCuO$_2$ and $Y_2BaCuO_5$ do exist even after sintering stage. Since the vacuum calcination method removes CO$_2$ when it is liberated, thus preventing formation of undesirable phases, this method was adopted for preparation of samples for further studies. Some changes incorporated at the sample preparation stage significantly improved the quality of the YBCO samples. These are (1) keeping the sample in an open boat instead of packing the sample powder in a partially closed cylinder (2) introducing an additional soaking stage at 600°C for another 24 hours. The samples prepared after incorporating these changes were found free from impurity phases and had a $T_c$ onset 89K. These samples were used for further studies which are discussed in later Chapters.
2.7 REFERENCES:


