CHAPTER 8

CONCLUSIONS AND SCOPE FOR FUTURE WORK.

In this chapter, the conclusions reached from the results of various experiments carried out on the oxygen non-stoichiometric Yttrium Barium Copper Oxide samples are summarised. During the course of the present work it was felt that a systematic preparation of large number of oxygen non-stoichiometric compounds was necessary for carrying out other physical property measurements. This would throw more light on the nature of this type of materials.

A zero back ground plate as sample holder made of Si(911) single crystal wafer for use in X-ray diffraction experiments, which would produce true intensities of the sample in the XRD pattern was developed. The XRD data generated using these Si(911) plates as sample holders, are found to be very clean with even back ground. The Bragg peak intensities in the experimentally recorded XRD patterns of powder diffraction standards match very well with the reported data. The data obtained by using Si(911) plates, when used with Rietveld refinement program, resulted in high figure of merit. The X-ray diffraction data of solid C\textsubscript{70} fullerene, generated with the use of these Si(911) plates, is now used as standard reference data and is incorporated in the powder diffraction data base published by International Centre for Diffraction Data (ICDD). The clean XRD patterns of the various \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x} \) samples in the present series of investigations using the Si(911) zero background plates allowed us to interpret the XRD results much more effectively than would have been possible with conventional sample holders.

The X-ray optics of the Siemens D 500 model powder diffractometer was tuned to an optimum resolution without sacrificing intensity. In the current setting the full
A new apparatus was designed and fabricated for electrical resistivity measurements of samples at high temperatures. This apparatus can be used either in vacuum or in an inert atmosphere. Using this apparatus, the resistance behaviour of several pure materials like graphite, platinum, tantalum et cetera was measured using a temperature profile in order to establish its performance. The results obtained from these experiments are in close agreement with those reported in the literature.

The high temperature resistivity measurement apparatus was used to investigate the resistance behaviour of the fully oxygenated YBCO sintered pellet sample using a temperature profile, in continuous flow helium gas atmosphere. Out of the several soaking temperatures studied, three cases with $T_A = 385°, 435°$ and $455°C$ are discussed in detail. The resistance of the sample showed steep increase from about $320°C$ during heating stage. This increase in resistance continued till about first 8 hours period of the soaking time, and thereafter the resistance tapered off in the soaking stage. The resistance change in the soaking stage could be fitted to a single exponential function for extracting a relaxation time ($\tau$) for the sample. The value of $\tau$ was found to be related to the soaking temperature $T_A$. This relaxation time $\tau$ varied from a few hours to several tens of hours depending on the soaking temperature $T_A$. It is interpreted that this relaxation behavior is due to the self diffusion of oxygen within the grains. The $\tau$ values obtained from these fits showed a good figure of merit indicating that the relaxation times obtained are highly reliable. Using these relaxation times, an Arrhenius plot was
generated and an activation energy of 0.7 eV was extracted. From the known diffusion constant of these materials, using the value of $\tau$ obtained from these studies, it was inferred that the diffusion lengths involved are about 14 microns, which is typically the size of the grains in these samples.

The resistance variation in the cooling stage showed a metallic behaviour. Depending upon the oxygen concentration $x$ of the sample (at the end of the soaking stage), the resistance continued to fall linearly upto a temperature $T_1$, where a change in the slope occurs. This is prominently seen for low $x$ values. This was followed by a further linear fall of resistance with temperature. The temperatures $T_1$ obtained in this study correspond to the temperatures $T$ associated with the formation of a pseudogap in the charge carrier excitation spectrum in underdoped superconductors known from other studies reported in literature. It is observed that all the samples investigated for high temperature resistivity studies are superconducting.

High temperature X-ray diffraction studies were carried out on the fully oxygenated YBCO samples, using an identical temperature profile in vacuum, unlike in high temperature resistivity studies where flowing helium gas was used. In all the cases studied, in addition to the peak shifts due to the thermal effects, the samples were found to undergo a rather abrupt phase transition from orthorhombic to tetragonal just above 320°C. The sample with $T_\lambda = 410°C$ showed interesting features. In this case the sample continues to lose oxygen even during soaking stage, the evidence of which is clearly seen in the soaking time curves. During the cooling stage the orthorhombic component increased, though marginally, with decrease in temperature. We attribute this to the ordering of the oxygen atoms in the basal plane of the sample. The XRD patterns of the
samples, investigated with other soaking temperatures, showed that the sample transformed to a tetragonal phase by the end of the heating stage. This phase persisted till the end of the experiment. The thermal expansion coefficients along different directions of the sample were extracted from the HTXRD data in cooling.

The HTXRD results indicate that due to oxygen diffusion the orthorhombic phase goes over to tetragonal progressively. On heating, oxygen was lost initially from the outer shell. Subsequently the oxygen atoms from inside the grains move towards the outer shell and the sample attains concentration equilibrium. The final sample consists of large portion of tetragonal phase together with a small portion of the orthorhombic phase, which was responsible for the metallic behaviour and superconductivity.

In the HTXRD studies, the samples with $T_A = 410^\circ$C and $390^\circ$C were found to be superconducting, whereas the sample with $T_A = 430^\circ$C was non-superconducting. These experiments reveal that for similar $T_A$ the final oxygen stoichiometry was smaller in the case of vacuum as compared to that in the helium atmosphere. In the high temperature resistivity studies, the end samples with $T_A = 430^\circ$C. and $455^\circ$C. were found to be superconducting. The only explanation one can offer is that the helium gas used, does contain a few ppm of oxygen, which plays a very crucial role in the oxygen stoichiometry fixation in the samples.

A comparison of the results obtained from high temperature resistivity measurements, TGA experiments, and the HTXRD studies is necessary for understanding the behaviour of the oxygen non-stoichiometric YBCO system. Here, it is to be kept in mind that, even though the temperature profiles used are similar, the TGA as well as high temperature resistivity experiments were conducted in helium
atmosphere, whereas the HTXRD experiments were carried out in dynamic vacuum using a diffusion pump.

The HTXRD curves during heating stage up to around 320°C. imply thermal expansion. This unitcell expansion ties up with the marginal weight loss (due to loss of oxygen) as seen from the initial portion of the TGA curve. Above 300°C. the rapid increase in resistivity as seen in the high temperature resistivity measurements and extending to about 8 hours of the start of the soaking stage are viewed as the changing over from orthorhombic system with higher oxygen concentration to another orthorhombic system with lower oxygen concentration together with slowly building up of tetragonal system. The HTXRD data in the soaking region supports this view. During initial portion of the soaking stage, the HTXRD Bragg peaks corresponding to (006)₀, (020)₀ and (200)₀ reflections show features of slow and continuous decrease in oxygen in the orthorhombic component. This feature of changes in peak positions do not continue after about 8 hours of the start of the soaking stage. Correspondingly, the high temperature resistivity curves show that the sample resistance slowly attains an equilibrium value by the end soaking stage. The HTXRD curves also shows a similar nature. That is, after a certain time, say about 8 hours from the start of the soaking, the peak positions of all the orthorhombic peaks remains more or less unaltered, till the end of the soaking stage. The TGA, curve also corroborates this view, as there is not much change in weight of the sample after about 8 hours from the start of the soaking stage.

During the cooling stage, the HTXRD curves shows continuous shifting of peak positions to higher angles corresponding to lattice contraction. In the TGA graph the curve in the cooling stage remains more or less constant indicating that there is no change in the sample weight (oxygen stoichiometry). On the other hand, in the resistivity
curves, the sample with $T_A = 435°C$, shown a non-linear behaviour, the signature of which is not observed in HTXRD or TGA experiments. Therefore, the beginning of the change of slope in the resistivity curves, which was interpreted as the signature of the pseudogap temperature ($T^*$), is a feature connected only with the charge carrier mechanisms in the system and is in no way related to structural or stoichiometric modifications.

From these observations, it is possible to formulate the following model. On heating a fully oxygenated YBCO sample, oxygen is lost from its basal plane slowly upto about 320°C, and thereafter the oxygen loss is rapid which depends on the temperature seen by the sample, till it reaches a soaking temperature $T_A$. This rapid loss of oxygen continues for some time during soaking stage. This is possible if oxygen is initially lost from the outer skin of the grains. During the soaking stage, the sample tries to attain an oxygen concentration equilibrium which is dependent on the soaking temperature $T_A$ chosen. In this process the oxygen atoms from core of the grains move towards the outer shell and a fraction of the volume of the grains becomes tetragonal. The final sample consists of larger portion of tetragonal phase together with a small portion of the orthorhombic phase. The orthorhombic component is responsible for the metallic behaviour and superconductivity.

During the X-ray characterisation of some of the heat treated YBCO samples in certain batches, it is found that the pattern contains several extra Bragg peaks in addition to the normal YBCO peaks. These additional peaks could not be assigned to any impurity phases. Some of these new peaks are found to be more intense than the normal (001) YBCO peak. Computer simulations were done for associating the new peaks with superstructures published in the literature. The peak positions match very well to a
supercell with unitcell dimensions, $4a_b4c$ where $a_b,c$ are the axial lengths of the normal unitcell. However, the calculated intensities of the Bragg peaks were not found to be in good agreement with the experimentally observed Bragg peaks. At this stage, fresh calculations were performed to generate a new pattern in which a few cations in the supercell were allowed to relax slightly. This has reduced the intensity difference to be within 5 - 10%. Since the XRD reveals the bulk property, the presence of ordered superstructure domains in a macroscopic scale is inferred.

**FUTURE SCOPE**

As the oxygen diffusion lengths involved in these materials are very small and diffusion times are very large, in order to produce completely equilibrated material, the time scales required are very large. It is also interesting to study the oxygen diffusion kinetics occurring along different crystallographic directions. Hence, it would be interesting to study resistivity ($\rho$) as a function of temperature on oriented thin films under similar temperature and atmospheric conditions similar to the ones used in these studies for understanding the behaviour of the material. Problems regarding production of completely ordered material on a macroscopic scale remain unsolved.

It is suggested that detailed studies should be carried out for determining suitable conditions for macroscopic development of ordered regions. To achieve this objective it is necessary to study various physical properties on well-ordered materials and redrawing the phase diagram taking into consideration the present knowledge of temperature and sample environment like oxygen partial pressure on these materials. Similar study on single crystals and oriented single crystalline thin films will be very useful in further illustrating the behavior of the system.