# CHAPTER - IX

# CHAPTER-IX

# CONCLUSION

The present work addresses the question of defect controlled charge transport in the grains as well as across the grain boundaries of the cuprate superconductors. We have thus examined the charge transport process in bulk and thick films of YBCO and its composites with Ag in Chapters IV to VIII. The present chapter summarizes the important findings from these studies.

## IX.1. Problem Addressed

Cuprate superconductors suffer from many types multidimensional imperfections: zero-dimensional (point defects; interstitials, vacancies of both cationic and anionic types, anti-site disorder etc.), 1-dimensional (linear dislocations), 2-dimensional (planar defects ; twin boundary, grain boundary), 3-dimensional (clusters of anionic disorder, voids, second phase precipitation and stacking faults) [1]. These defects are basically inherited from the very preparation conditions of the cuprates which, unlike most other oxides, can be prepared only at high sintering temperatures. This problem seems to be related to a lack of thermodynamic stability of the cuprates at low temperatures. The complex phase diagram specifies the reactants and the reaction conditions that can lead to a particular phase, it also permits the formation of other metastable phases if conditions of preparation are slightly altered. Most of these phases show superconductivity over a broad range of compositions and hence are defect ridden.

The defects that make the very existence of superconductivity possible in cuprates, also drive these systems away from equilibrium by way of lattice mismatch and coordination incompatibility at the various cation sites. Since the discovery of superconductivity in cuprate, it has been speculated by many that metastability is inextricably associated with the mechanism of superconductivity. We probe into a possible microscopic mechanism of the evolution of metastability in the cuprates and its influence on the superconductivity of YBCO when the oxygen deficiency, y varies in the range 0 to 1, and when this system is doped with trivalent and monovalent ions in its charge reservoir layer (Chapter IV).

The doping of monovalent ion Ag in the structure of YBCO and the corresponding solubility limit in particular has been controversial due to the following reasons. Ag is a noble metal and has a 2-fold oxygen coordination. Most often it segregates to the grain boundaries and influences the microstructure of the cuprates. Even when it is incorporated in the grains, its site specific occupancy and its fixed two fold oxygen coordination demands a crucial control over the preparation conditions like the sintering temperature and the atmosphere during sintering. Thus, there exist several conflicting views in the literature on the effect of Ag doping in YBCO on the structural parameters and the superconducting transition temperature, Tc of the later. This problem is addressed in Chapter-V.

One of the crucial problems for application of the cuprate superconductors as well as for the fundamental understanding of charge transport in these systems is the inherent granularity in them. Unlike their classical counterparts, the grain boundary issue becomes prominent in cuprates because of their much shorter coherence length, high superconducting anisotropy and reduced dimensionality [2]. The superconducting state of the HTSC is depressed at the grain boundaries and the phase coherence of the neighbouring grains is established by the Josephson tunneling across the weak links found at the grain boundaries. Due to the current frustration arising across the misaligned grain surfaces of highly anisotropic randomly oriented grains and sample defects such as cracks and voids, current conduction becomes percolative in the granular cuprates [3-5]. The conventional imaging technique have been found to be inadequate to probe into slight crystallographic misalignments which can have a dramatic influence on the overlap of superconducting wave functions across the grain boundary. This is further aggravated by the very short coherence length of the cuprates leading to diminished critical current. Control of granularity in these systems therefore has involved controlling several aspects as grain alignment, grain growth, sample defects and second-phase formation. The grain boundaries being a natural consequence of the very preparation conditions of the cuprates, they cannot be completely eliminated. They remain in the samples to a sizable fraction and limit the applicability of these ceramic superconductors. The attempts by various authors therefore have been restricted to characterizing the various forms of granularity in the cuprates and controlling them through sintering schedules and by composite formation with noble metals like silver and gold. Chapter-VI and VII address this problem and propose methods for characterizing, quantifying and controlling the granularity in bulk and thick films of YBCO/Ag composites.

Considering the importance of the various types of chemical and structural disorder in influencing the superconductivity in the cuprates, a large number of authors have studied the evolution of superconductivity with defects and disorder introduced artificially into the cuprate structure. The methods used for the purpose include doping the cuprates with foreign atoms, intercalation/deintercalation of oxygens, quenching from high temperatures, ion irradiation etc. Since irradiation provides a possibility to vary the state of disorder in enormous proportions from the most delicate degrees of defect formation up to highly disordered and possibly amorphous states, a large number of studies have been devoted to understand the modification of superconducting and normal state properties brought about by irradiation induced defects. The response of the cuprate systems to ion irradiation to a large extent has been shown to depend on the initial quality of the sample. The initial quality in turn depends on the type and concentration of the intrinsic defects present prior to irradiation which control the evolution of the system during irradiation [6]. In this context, the granularity of the cuprates has posed a severe constraint on isolating the effect of irradiation on grains and grain boundaries [7]. Therefore, even though a large number of studies have been devoted to this field of research a unanimous picture on the effect of irradiation on superconductivity and normal state properties is yet to emerge. Chapter-VIII addresses the problem of irradiation induced modifications in granular cuprate superconductors.

## IX.2. Techniques Used and Facilities Developed

The different techniques used for the characterizations of the cuprate superconductors prepared in our laboratory are :

1- AC magnetic susceptibility measurement from room temperature (RT) to 10 K,

2- DC four probe resistivity measurement from RT to 10 K,

3- Superconducting critical current Jc measurement,

4- Oxygen content determination,

5- Particle induced x-ray emission,

6- Powder x-ray diffraction,

7- Optical imaging,

8- Scanning electron microscopy.

Some of the facilities developed for the preparation and characterization of the samples used in the present study include :

1. Facilities for preparation of bulk and thick films of granular sintered YBCO and YBCO/Ag composites. These facilities involved sample weighing, mixing and solid state sintering under varying atmospheric conditions for bulk samples, and screen printing, dip coating and doctor balding with diffusion reaction of an overlayer on the substrate for thick films.

2. Computer controlled data acquisition for the measurement of D.C. resistivity, A.C. magnetic susceptibility and superconducting critical current as a function of temperature down to 10 K. The instruments used for the purpose are : constant current source, nanovoltmeter, reed-relay card for resistivity and critical current measurement, and lock-in amplifier, power

amplifier, mutual inductance bridge for the susceptibility measurement. For the variation of temperature from RT to 10 K, a closed cycle He refrigerator and a temperature controller was used. Some of the instruments had IEEE-488 GPIB interface while others had RS-232 interface for computer interfacing. Programs for data acquisitions (Appendices) were thus developed for data acquisition involving both kinds of interfaces.

3. To measure off-line and on-line resistivity of the samples while they are irradiated with swift heavy ions from the pelletron accelerator at the Nuclear Science Centre, New Delhi, we developed for the first time, a facility to measure the temperature dependence of resistivity of four samples simultaneously during a single run. In the process, precious time of the accelerator can be saved and the allotted beam time can be effectively utilized.

4. An iodometric titration setup was developed for determination of oxygen content in the different bulk superconductors prepared in the laboratory.

## IX.3. Important Findings

Our crystallochemical analysis of oxygen deficient and tri/monovalent ion doped YBCO presented in Chapter-IV reveals a possible mechanism of the evolution of metastability in the cuprates by way of coordination incompatibility and charge state instability in the charge reservoir layer of this system. We show in particular that the existence of these metastable states are a necessity for the occurrence of antiferromagnetically coupled spin fluctuations in the $CuO_2$ planes and hence for the very existence of superconductivity in the cuprates. The detailed analysis of the evolution of charge and spin degrees of freedom with oxygen vacancy concentration has explained the two plateau structures (90 K and 60 K) of the Tc vs oxygen content in YBCO with a Tc peak in the first plateau at an oxygen content less than 7. The spatial equilibration of the unstable 3-fold oxygen coordinated Cu(1) sites to stabler 4-fold and 2-fold ones explains the independence of hole concentration on oxygen deficiency when the later exceeds a certain critical value and accounts for the 60 K plateau.

In the case of trivalent and monovalent ion doping of YBCO, our crystallochemical analysis specifies the carrier concentration dependence on dopant concentration and provides an explanation for the observed structural phase transition from the orthorhombic to tetragonal phase. The applicability of this analysis is examined in a series of Ag doped YBCO in Chapter-V. We show that the fixed 2-fold oxygen coordination of the Ag necessitates preparation of the samples at a relatively lower sintering temperature and ambient atmospheric condition to prevent Ag precipitating at the grain boundaries. The effect of Ag doping on the lattice parameters and Tc then becomes a natural consequence of its effect on the oxygen content in YBCO due to its fixed 2-fold oxygen coordination. The fixed two fold oxygen coordination of Ag also provides rigidity to the CuO chains and prevents oxygen in/out diffusion as evidenced from quenching experiments.

Analysis of the temperature dependence of normal state resistivity in a series YBCO/Ag composites (Chapter-VI and VII) enabled us to quantify the extent of granularity in these systems in terms of weak-link resistivity across grain boundaries and the current percolation factor arising from the misaligned grains and sample dependent defects such as voids and cracks. Evolution of these parameters with Ag vol.% in these systems clearly established that more than residing at the grain boundaries and participating in the current percolation, Ag brings about microstructural modifications in the composites. One of the consequences of the microstructural modifications is better grain alignment and reduced voids and cracks. These effects are shown to be prominent in YBCO/Ag composite thick films where film thickness approaches the dimension of the grains. The very preparation procedure adopted for thick film growth, i.e. diffusion reaction of an overlayer of $Ba_3Cu_5O_8$/Ag on a $Y_2BaCuO_5$ substrate provides a semiliquidous phase at the sintering temperature and also aids in grain alignment effect. Our studies on the paracoherent resistivity below Tc, the branching point from the dissipative to non-dissipative state in the normal to superconducting transition region, the excess conductivity above Tc and the associated exponents establish that current conduction in these systems is essentially percolative in nature. Based on the variation of the granularity parameters with Ag vol.%, a grain growth mechanism leading to larger grains with narrower size distribution in the composites is proposed.

The current percolation model proposed in Chapter-VI has been extended to probe the evolution of microstructure of a granular medium under swift heavy ion (SHI) irradiation. From the temperature dependent in-situ resistivity measurement during ion irradiation, we have been able to isolate the irradiation induced modifications at the grain boundaries and the grains and probed into the evolution of the microstructure with irradiation fluence and energy. With 120 MeV S ion irradiation, we show that in addition to damaging the insulating grain boundaries and hence destroying superconducting phase coherence, ion irradiation brings about an improvement in the microstructure of the cuprates. Irradiation is shown to induce alignment of the grains in an otherwise randomly oriented granular superconductors. The 250 MeV Ag ion irradiation with $S_e > S_{eth}$ is expected to completely suppress superconductivity in YBCO beyond a critical fluence $\phi_c$. where amorphized latent tracks start overlapping. Contrary to this expectations, we observed the suppression of Tc by about 10 K even when the irradiation fluence was an order of magnitude less than $\phi_c$. We explain this unusual behaviour based on a mechanism of ion-matter interaction which involves the creation of atomic size point defects due to secondary electrons emitted radially from the ion tracks when the samples are irradiated at low temperatures. This process, with a much larger interaction cross section than ordinarily expected without taking these electrons into consideration, accounts for the observed Tc decrease in the low fluence regime of SHI irradiation.

## References


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