Chapter 1

INTRODUCTION

During the ten years since the discovery of high temperature superconductivity in La-Ba-Cu-0 system with critical transition temperature of 30 K by Bednorz and Miiller in 1986; an enormous amount of experimental and theoretical effort has been expended leading to a considerable advancement in our understanding of these materials. However, a clear understanding of the mechanism of high temperature superconductivity remains elusive. This chapter is intended to provide a short discussion on the historical background and basic properties of superconductors followed by a brief review of various developments in the field of high $T_c$ superconductivity. Finally, the motivation for the studies presented in this thesis is discussed.

1.1 Historical background on superconductors

Helium was discovered on earth in 1895 by William Ramsay. Kammerling Onnes succeeded in liquifying helium gas at 4 K in 1908. Using liquid helium, he proceeded to investigate the electrical resistivity in various metals as a function of temperature. In 1911, he discovered that the electrical resistance of mercury suddenly dropped to zero whenever the sample was cooled below 4.2 K [1]. He called this new phenomenon i.e., the absence of resistance below a critical temperature, as superconductivity; and that temperature the critical temperature, $T_c$. A year later, Onnes reported that an applied
magnetic field \( (H_c) \) as well as a sufficiently strong electric current can destroy the superconductivity.

Meissner and Ochenfield [2] in 1933, discovered another distinct property of the superconducting state called the perfect diamagnetism. They found that the magnetic flux is expelled from the interior of the sample if a superconductor is cooled in a weak magnetic field to below superconducting transition temperature. This phenomenon is called the Meissner effect.

In an effort to find superconductors with higher critical temperatures, early researchers investigated many other metals and metallic alloys. Several metals like Nb and alloys like \( \text{Nb}_3\text{Ge} \) were found to be superconducting. In 1986, the highest critical temperature superconductor was \( \text{Nb}_3\text{Ge} \) with \( T_c \) 23 K.

Several experimental studies have been carried out to study various properties of the superconductors. Alexei Abrikosov studied the behavior of superconductors in an external magnetic field and discovered that one can distinguish two types of materials: type-I and type-II superconductors. Superconducting materials that completely expel the magnetic flux until they become completely normal are called type-I superconductors. Above the critical field \( (H_c) \), the superconductor is normal and magnetization \( M = 0 \). For a type-II superconductor, there are two critical fields; the lower \( H_{c1} \) and the upper \( H_{c2} \). The flux is completely expelled only up to the field \( H_{c1} \). Above \( H_{c1} \), the flux partially penetrates into the material until upper critical field \( H_{c2} \) is reached. Above \( H_{c2} \), the material returns to the normal state. Between \( H_{c1} \) and \( H_{c2} \), the material is said to be in mixed state.

From the specific heat measurements as a function of temperature, it was found that
specific heat shows a jump at $T_c$ together with the more rapid decrease with decreasing temperature. This decrease is proportional to $\exp(-A/T)$ in the superconducting state and suggestive of excitation of carriers across an energy gap, $A$ [3].

In 1962, Brian Josephson postulated a quantum tunnelling effect that should occur when a supercurrent tunnels through an extremely thin layer (as $10\AA$) of an insulator. His predictions were confirmed in a year and the effects are known as the Josephson effects [4].

Many phenomenological theories have been proposed to explain the experimental results. Taking the transition between the normal and superconducting states as reversible and by applying the general principles of thermodynamics to the transition, the expressions for Gibb’s free energy, entropy and specific heat in the normal state and superconducting state in terms of field and temperature were derived. The entropy in the normal state is greater than the entropy of the superconducting state, which shows that the superconducting state is a more ordered state. Entropy change is continuous and specific heat shows a discontinuity at the transition, which implies that superconducting to normal state transition is a second order transition in the absence of the magnetic field, while it is first order in the presence of the field.

In 1935, London proposed a classical model of superconductivity. This theory essentially incorporates the fundamental superconducting properties of zero resistance and perfect diamagnetism into electromagnetic constitutive relations known as London equations [5]. This model explained the Meissner effect and predicted the penetration depth $\Lambda$: this is a characteristic length of penetration of the static magnetic flux into a superconductor. While the interior of a pure superconductor expels the magnetic flux and is, therefore, flux free (perfect diamagnetism), the static flux persists within a sheath of
depth A at the surface of the sample and its magnitude decreases towards the core of the superconductor.

In 1950, Ginzburg and Landau developed a remarkable phenomenological theory of superconductivity that integrates *electrodynamic*, quantum mechanical and *thermodynamic* properties of superconductors. They have taken the complex wave function of superelectrons as the order parameter and introduced a new parameter called the ‘coherence length’ [3]. *Coherence* length is defined as the characteristic length scale over which the order *parameter* changes to produce the condensation *energy*.

Despite their utility, the models discussed above are phenomenological in nature. In other words, these models do not give any explanation as to how superconductivity occurs.

In 1957, Bardeen, Cooper and Schrieffer developed the theory that provides microscopic explanation for superconductivity [6]. The basis of this theory is that the electrons that carried lossy currents in the normal state pair together in the superconducting state. These pairs which carry lossless supercurrents are called Cooper pairs. The effective unit of charge of a cooper pair is 2e rather than e. Like in conventional superconductors, it has been established by Gough *et al* [7] that the effective unit of charge in high *Tc* superconductors is 2c.

### 1.2 High Temperature superconductors

In 1973, Johnson by discovering superconductivity in Li-Ti-O$_3$ at temperatures as high as 13 K, removed the belief that superconductivity in the oxide materials was limited to very low temperatures [S]. In 1975, superconductivity was discovered in BaPb$_{1-x}$Bi$_x$O$_3$
at around 14 K to report another member to the growing class of superconducting oxides [9]. In 1986, the first high temperature superconductor La-Ba-Cu-O with $T_c$ of 30 K was discovered by Bednorz and Müller [10]. Takagi et al [11] confirmed that La-Ba-Cu-0 had the tetragonal $K_2NiF_4$ structure. Uchida et al [12] found the exact composition of the superconducting phase. Jorgenson et al [13] reported the crystal structure from neutron diffraction study of these samples. They reported that this structure had copper ions coordinated to four oxygen in a square plane and two O atoms along c-axis to form an octahedral coordination. The parent compound La$_2$CuO$_4$ is an antiferromagnetic insulator with orthorhombic structure. Superconductivity can be achieved by replacing La in this parent compound with alkaline earth metal (example Sr) [14] or by forcing excess oxygen into the compound [15]. For La$_{2-x}$Sr$_x$CuO$_{4-y}$ system, the $T_c$ is optimal ($\approx$ 36 K) for $x = 0.15$ [16]. Several substitution effects have been studied in La$_{2-x}$Sr$_x$CuO$_4$ system. The 3d transition metal ions at Cu site depresses the $T_c$ very rapidly [17, 18]. This suggests the importance of Cu-0 planes in superconductivity.

Superconductivity in Y-Ba-Cu-0 (Y-123) superconductors was discovered by Wu, Chu and coworkers in 1987 with $T_c$ about 92 K [19]. The composition of the phase was found to be $YBa_2Cu_3O_{(7-\delta)}$ [20-21]. The crystal structure has been reported by many groups [22-24]. The structure of the superconducting material is orthorhombic. There are two sites in the unit cell; the copper in the Cu-0 oxide plane and the copper in the Cu-0 chain. The parent compound $YBa_2Cu_3O_6$ is antiferromagnetic insulator with tetragonal structure [25].

The properties of this system are very sensitive to oxygen content [26,27]. The compound undergoes an orthorhombic-tetragonal transition at elevated temperature [28]. The substitution of Yttrium by other rare-earth elements (except for Pr, Ce and Tb) do
not affect superconductivity [29-35]. Substitution of 3d transition metal ions at Cu-site suppresses the $T_c$ rapidly [36-41].

Two other superconducting phases in the homologous series of compounds having formula $Y_2Ba_4Cu_{6+n}O_{14+n}$ namely $YBa_2Cu_4O_y$ ((124) with $n = 2$) [42-44] and $Y_2Ba_4Cu_7O_y$ ((247) with $n = 0$) [44] were identified with $T_c$ of 80 K and 40 K respectively. Their crystal structures are also reported [45]. Migatake et al reported $T_c$ of 90 K in $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_y$ system [46].

Superconductivity in Bi-Sr-Cu-0 system was discovered in 1988 by Michel et al [47] with $T_c$ around 20 K. Superconductivity was subsequently discovered in the related Bi-Sr-Ca-Cu-0 systems by Macda et al [48]. Three superconducting phases have been identified with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ with $n = 1, 2, 3$ and having $T_c$s 10, 85 and 110 K respectively [49-53].

Superconductivity in Tl-based compounds was discovered by Sheng and Herman [54]. Two homologous series of superconducting compounds have been reported in the Tl-Ba-Cu-0 system [55-63], the compositions of which may be noted as $Tl_mBa_2Ca_{n-1}Cu_nO_{2(n+1)+m}$, where $m = 1$ or 2 and $n$, the number of CuO$_2$ planes upon which superconductivity occurs ranging over $n = 1$ to 4 for $m = 1$; and 1 to 3 for $m = 2$. These two series of cuprates contain the compounds with highest known $T_c$ of 125 K for $m = 2$, $n = 3$ [58] and 122 K for $m = 1$, $n = 4$ [63]. The structures of Tl-compounds are similar to that of Bi-compounds except for c-axis lengths.

Cava et al [64] reported a new family of superconductors with the general formula $Pb_2Sr_2ACu_3O_{8+\delta}$ ($A = Y$, rare-earths, Ca, Sr) with $T_c = 70$ K.
The electron doped superconductors with formula $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$ (Ln = Nd, Ce, Pr, Sm, Eu; M = Ce, Th) were discovered with critical temperatures as high as $25\text{ K}$ for $x<0.15$ and $y<0.02$ [65-67]. In this family of superconductors, electrons are the charge carriers unlike other Cu-oxide based superconductors in which holes are the charge.

The discovery of conductivity in $\text{A}_x\text{C}_6\text{O}_{10}$ (where A represents an alkali metal) [68] and superconductivity in $\text{K}_x\text{C}_6\text{O}_{10}$ [69] has been followed by reports of superconductivity in other alkali-metal doped fullerides with transition temperatures as high as $33\text{ K}$ [70].

Superconductivity at about $94\text{ K}$ has been discovered in $\text{HgBa}_2\text{CuO}_4$ (Hg-1201) by Putillian et al [71]. Schilling et al reported a $T_{c(\text{onset})}$ of $133\text{ K}$ in \text{Hg-Ba-Ca-Cu-O} system [72].

Recently, Nagarajan et al reported superconductivity in borocarbide system Y-Ni-B-C with $T_c$ around $12\text{ K}$ [73].

### 1.3 Bi-Sr-Ca-Cu-O superconductors

The superconductor $\text{Bi}_2\text{Sr}_2\text{CuO}_y$ (2201) is the first of a series $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ of modular layered structures in which copper and oxygen in sheets, typical of all high $T_c$ materials, are spaced by alkaline earth cations, and interlayered with $\text{Bi}_2\text{O}_2$ layers. In $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) the Cu-0 sheet in Bi-2201 is replaced by $\text{CuO}_2/\text{Ca}/\text{CuO}_2$ sandwiches and in the case of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) the additional $\text{CuO}_2$ and Ca layers are inserted within the $\text{CuO}_2/\text{Ca}/\text{CuO}_2$ sandwich of Bi-2212, yielding a $\text{CuO}_2/\text{Ca}/\text{CuO}_2/\text{Ca}/\text{CuO}_2$ sandwich.
Though the basic topology is simple, these structures are always complicated by stacking faults, modulations and oxygen and cationic disorder. Different types of unit cells with different unit cell parameters have been reported in the literature [74-79]. The crystal structures reported by Tarascon et al [52] are shown in Fig. 1.1. They assumed pseudo tetragonal symmetry and reported the unit cell parameters (a, b and c) for the three crystal structures; a ~ b ≈ 5.4 Å and the c values are 24.6, 30.6 and 37.1 Å respectively for the three systems.

The 2201 structure consists of a corner linked plane of Cu square coordinated by O1 (Cu-O1 = 1.9 Å), sandwiched between two Sr-02 layers. The 02 oxygens lie immediately above and below each oxygen (Cu-02 = 2.6 Å), thus forming an extremely elongated CuO$_6$ octahedron. Strontium has nine nearest oxygens with an average Sr-0 distance of ~ 2.7 Å. The SrO/CuO$_2$/SrO module is sandwiched between BiO$_2$ bilayers in which bismuth adopts a very distorted octahedral coordination. Four Bi-03 bonds near the (001) plane range from 2.2 to 2.8 Å, while the Bi-02 bond linking Bi to the Sr-02 layer is much shorter (about 2.0 Å). In contrast, the sixth Bi-03 bond which joins the adjacent sheets in Bi$_2$O$_2$ bilayers is longer than 3.0 Å. This long and weak Bi-03 bond parallel to the c-axis results in very much weak interlayer bonding and mica like behavior in all the Bi-superconductors.

In 2212 structure, Ca adopts eight coordination similar to Y environment in Y-123. There are no oxygen atoms at this level, so copper atoms have only five nearest neighbors in square pyramidal coordination rather than the elongated octahedral coordination of 2201. The structure slab containing SrO/CuO$_2$/Ca/CuO$_2$/SrO is topologically identical to YBa$_2$Cu$_2$O$_6$ (122) module portion of the Y-123 structure.
Fig. 1.1 Crystal structure of the three superconducting phases of Bi-Sr-Ca-Cu-O superconductors
In 2223 the outer Cu2 atoms are in square pyramid coordination as found in Y-123 and 2212, while the Cu1 atoms are in square planar coordination.

Substitutional studies at Cu site [80-84] have been reported in this system. The substitution at Cu site is found to suppress the superconductivity very fast. This indicates the importance of Cu-0 planes for superconductivity in these systems.

1.4 Motivation for the present work

It is generally realized that the physical properties of the CuO2-based superconducting systems are strongly related to the carrier concentration [85]. Fig. 1.2 shows the model phase diagram for high Tc superconductors. The parent materials i.e., the systems corresponding to left end of the phase diagram are charge-transfer insulators with long range antiferromagnetic ordering. Charge carriers are introduced into the parent material by doping, while hole carriers can be introduced by either cationic doping or oxygen intercalation. Upon doping, the antiferromagnetic ordering collapses dramatically and gives way to superconductivity. The effectiveness of holes in destroying the magnetic order is interpreted as follows. The holes, which mainly enter into the oxygen 2p orbital, are quite effective in frustrating the antiferromagnetic (AF) coupling between the Cu spins. For a certain range of hole concentration, this leads to the formation of spin-glass state at low temperatures. Neutron-scattering experiments indicate that AF correlations does persist in the superconducting state, but the AF correlation length is much shorter. At a certain critical doping concentration, the system undergoes an Insulator-Metal (M-I) transition and superconductivity emerges.

With increase in the hole concentration, the superconducting transition temperature
Fig. 1.2 Model phase diagram of the high $T_c$ cuprate system
\( (T_c) \) increases and reaches a maximum, and further increase in hole concentration leads to a decrease in \( T_c \) and the sample becomes a non-superconducting metal. The composition which gives the maximum \( T_c \) for a given system is called 'optimally doped'. The lower carrier density side of the \( T_c \) maximum is called 'underdoped' and the higher carrier density side of the \( T_c \) maximum is called 'overdoped' regions.

Briefly, one can say that the fully metallic overdoped region is Fermi liquid like, while the undoped material is insulator. The questions of fundamental importance are, how to explain the nature of the intermediate phase (superconducting phase), the change in electronic structure of \( \text{CuO}_2 \) planes as the carrier (hole) density increases and the observed MI transition. To get the answers to these questions, various physical properties have been studied theoretically and experimentally. Among these, the transport property experiments are very sensitive probes to get useful information about the electronic structure and serve as a test for theories.

In this process, many studies on transport coefficient measurements like resistivity and thermoelectric power (TEP) have been made in various systems [85, 86]. TEP measurements provide not only the information complementary to resistivity, but they are also more direct probes to the intrinsic properties of polycrystalline materials because TEP is less sensitive to the grain boundary effects than the electrical resistivity. It is an interesting transport coefficient which can provide information about the concentration and sign of the carriers and the band structure of the material.

\( \text{YBa}_2\text{Cu}_3\text{O}_y \) exhibits a larger nonstoichiometry for \( y = 6 \) to \( 7 \) and its physical properties are strongly dependent on the oxygen content \( (y) \) [26,27]. It undergoes a transition from superconductor to semiconductor with decreasing oxygen content [28]. Whereas in
Bi-based cuprates, the oxygen content is relatively stable with respect to substitutions under the same conditions of sample preparation and the fundamental crystal structure remains unchanged during the Superconductor-Insulator transition. All the Cu sites in these cuprates are equivalent and its modulation structure is not influencing the superconductivity of the system [87]. So, the observed changes in the physical parameters can be explained by taking dopant concentration as the monitoring parameter.

In $\text{YBa}_2\text{Cu}_3\text{O}_7$ except Pr, Ce and Tb, all other rare-earth substitutions at Y-site hardly affect the superconductivity [29-35]. These three elements have the common feature that they can exist both in +3 and +4 valence states. The Ce and Tb substitutions lead to the formation of multiphases in $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123) system, while in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ system, $T_c$ decreases and vanishes at around $x = 0.5$ [88].

In $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (Bi-2212) system also, several reports have described the effects of rare-earth replacing Ca or Sr ion [89-95,96-99]. However, only a few studies on Pr [100-103] and Ce [99, 103-105] substitution effects and none on Tb doped Bi-2212 system have been reported to our knowledge. Moreover, no TEP studies have been reported on Pr, Ce and Tb doped Bi-2212 system. Therefore, a systematic study on the effect of substitution of these elements in Bi-2212 system has been undertaken, which might give an information about the valence state of these ions, the crystal structure and the relation between the normal state properties and $T_c$. The present studies were undertaken with the following objectives.

1. To synthesize samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_y$ ($\text{M} = \text{Pr}, \text{Ce} \text{and} \text{Tb}$) systems and find out the solid solubility limit of each dopant.
2. To characterize the synthesized materials for phase purity and estimate the lattice
parameters from the X-ray diffraction (XRD) studies. To study the effect of dopant ion on the crystal structure of Bi-2212 system.

(3) To measure AC susceptibility of the samples in order to find out bulk $T_c$ and its variation with dopant nature and content.

(4) To undertake detailed resistivity measurements on the Pr, Ce and Tb doped Bi-2212 system to understand the effect of rare-earth substitution on $T_c$ and normal state properties. To understand the nature of conduction in the semiconducting samples of the present systems.

(5) To undertake the study of temperature variation of TEP of the Pr, Ce and Tb doped Bi-2212 system so as to obtain information about the band structure of these materials and ascertain the validity of various theoretical models to the TEP experimental data.

Second chapter contains the details about the experimental techniques employed in the present studies.

Third chapter describes the sample preparation and their characterization by X-ray diffraction and AC susceptibility.

Fourth chapter contains the detailed resistivity studies and the analysis.

Fifth chapter contains the TEP studies and the analysis.

Sixth chapter describes the summary of the results and conclusions arrived at from the present studies.
1.5 References


85. Y. Iye in Physical properties of high temperature superconductors ///edited by D. M. Ginsberg (World scientific, Singapore) (1992) and references therein.