ABSTRACT

While the unusually high transition temperatures of the recently discovered oxide superconductors were the main cause of such wide spread excitement in the early stages of their discovery, from the physics point of view, this discovery was associated with a number of surprises. The biggest of these surprises is that these materials basically belong to a family of compounds that are insulating and magnetic. Their properties are governed by narrow d-bands, where electron correlations, exchange effects, electron-phonon effects etc. dominate. Indeed, not only the superconductivity of these materials is very different from the conventional superconductors for which BCS theory has proved very successful, but the normal state properties especially transport properties already show that these materials can not be understood in terms of traditional metal theory. Currently there is a lot of effort to resolve the issues connected with the normal state properties, as these hold the key to our eventual understanding of the superconducting state.

In this thesis, we have studied in detail the thermoelectric power (TEP) of Bi-based superconductors. The Bi-based superconductors have distinct advantages over other series of oxide superconductors. They have higher transition temperature than RE-based superconductors (RE-Ba-Cu-O) and have less atmospheric degradation. They are also easier to handle than Tl-based
superconductors (Tl-Ba-Ca-Cu-O) because of toxic nature of the later.

Though the Bi-based superconductors are superior to other oxide superconductors, still they have a major problem of multiphase formation. Bi-based superconductors exhibit three superconducting phases namely $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ corresponding to three values of n (n=1,2,3). Transition temperature of these superconductors increases with increasing value of n from 1 to 3, being 20K, 80K and 110K for n=1,2,3 respectively. Formation of pure high $T_c$ phase (110K) phase is very difficult. Most of the time it is associated with the formation of other two phases with a small fraction of 110K phase. We optimized the conditions and compositions for higher fraction of 110K phase, by varying the concentration of different components of the system, varying the oxygen content etc. Once the conditions are optimized, substitutions like Sb and Li are tried. Effect of silver addition has also been studied in detail.

Resistance and TEP of these specimens are measured. TEP of these materials is positive, increases linearly with decreasing temperature and shows a hump before going to zero at transition temperature. TEP shows either a tendency of changing sign or changes sign to negative at about 300K. This behaviour of TEP cannot be explained in terms of simple metallic theory, where TEP ($S$) is given as a combination of diffusion component (AT) and
phonon-drag component \( \frac{B}{T} \) i.e. \( S = AT + \frac{B}{T} \). According to conventional metallic theory sign of \( A \), in general, represents the sign of charge carriers and phonon drag component shows a peak between \( \theta_D/5 \) and \( \theta_D/10 \) (\( \theta_D \) is Debye temperature). Applying the above formula to these superconductors one finds a negative and low value of \( A \), and large positive value for \( B \). Negative sign of \( A \) is contradictory to the sign of charge carriers indicated by Hall coefficient. Moreover, the hump observed at about 120K is not likely to be a phonon-drag maxima (as \( \theta_D \approx 400K \) for these superconductors). These features of TEP thus can not be explained by the above formula and TEP shows deviations from this formula below 160K. In view of this unusual behaviour of TEP, we have examined the situation in the light of marginal Fermi liquid (MFL) hypothesis. We find that much of our data in the temperature range of 130K to 300K can be fitted quite successfully to a formula derived using MFL hypothesis.

Another aspect investigated in this thesis is related to percolation of thermoelectric power. This is not quite related to nature of superconductivity in these materials, but is interesting in view of some rather unexpected features. TEP of many samples of these superconductors show a large difference in zero resistance temperature and zero TEP temperature. Further under certain conditions of preparation, when the fraction of superconducting phase in the sample is very small (smaller than
percolation fraction) there are reports of vanishing TEP at the transition temperature of the pure sample. We surmise that both these observations can be attributed to different nature of percolation of TEP, as was suggested by Jha et al. The percolation aspects of TEP in inhomogenous superconductors have been investigated in some theoretical detail here.

In first chapter of the thesis we give a brief introduction of the discovery of high temperature superconductivity along with the structures of the different series of high $T_c$ compounds. Transport phenomenon has been reviewed with emphasis on thermoelectric effects. A brief survey of different contribution to TEP is presented and the main features of TEP of various systems like metals, alloys, semiconductors and superconductors is discussed. Towards the end of first chapter, TEP data reported on high temperature superconductors has been reviewed. The observations of lower percolation threshold for TEP reported for different systems are described.

Second chapter summarizes the basic techniques for sample preparation, characterization, resistance and TEP measurements. Samples are prepared using solid state reaction method. X-ray diffraction (XRD) and scanning electron microscope (SEM) are the basic techniques for characterization of the specimens. XRD patterns are recorded on Siemens D-500 X-ray powder diffractometer using CuK$_\alpha$ radiations in 2$\theta$ range of 3$^\circ$ to 45$^\circ$. SEM
micrographs are taken on the fractured surface of the specimens using Jeol-35CF scanning electron microscope. Resistance is measured using four probe method in the temperature range of 77 K to 300 K for all the specimens. TEP is measured using differential (incremental) method in the temperature range of 70 K to 300 K.

Experiments carried out in order to optimize the preparation conditions and compositions are given in third chapter. Effect of oxygen has been studied by annealing the specimens in air and in vacuum with various concentration of PbO added to the Bi₂Sr₂CaCu₂O₈. Resistance measurements and XRD results clearly indicate the role of oxygen to be dependent on the Pb concentration and Pb is essential to obtain 110 K phase in these systems. Then we have studied the effect of substitution of Bi in small amounts by Pb, varying the concentration of Pb in the formula Bi₂₋ₓPbₓSr₂Ca₂Cu₃O₈ (x varying from 0.0 to 0.5). Results indicate the Pb concentration of 0.3 and 0.4 give rise to formation of larger volume fraction of high Tc phase. Using these two concentrations of Pb, Sr concentration is varied from 2.0 to 1.4. Sr concentration of 1.6 gives rise to the formation of pure 110 K phase. Specimens are annealed in different atmospheres to study the effect of oxygen concentration. Oxygen and air annealing at 500°C does not change the quality of the specimens but vacuum annealing at the same temperature degrades the quality of the specimen and results in the reduced formation of 110 K phase.
Next we have studied the effects of doping of the above parent compound by Sb and Li. Transition temperature of these oxide superconductors changes either by a change in carrier concentration or by a change in structure. Doping by Sb which belongs to the same group in periodic table as Bi does, should change the structure of these compounds mainly and Li which is in +1 valence state (valence state of Bi is +3 or +5) should change the carrier concentration mainly. The results of these doping studies are reported in chapter IV. Sb doping does not result in an increase in transition temperature as reported by several groups, but a new Cu-deficient phase is formed. Li doping decreases the zero resistance temperature of the system and decomposes the high $T_c$ phase.

$\text{TEP}$ of these specimens has been fitted to the formula obtained using marginal Fermi liquid hypothesis. The data fits rather nicely to the formula and enables us to obtain some other parameters like Fermi energy, coupling constant, cutoff-frequency from these fits along with fits to resistance data. These fittings indicate a rather small phonon drag component.

Oxide superconductors are ceramics and are very brittle, hence can not be drawn in the form of wires as such. For making wires one needs a suitable cladding material. Silver is proven to be a good cladding material for RE-based superconductors as Ag addition up to 60 wt% addition does not degrade the transition
temperature. But for Bi-based superconductors contradictory results have been reported. In view of these rather large disagreement on the effect of Ag addition to Bi-system, we carried out studies on the effect of Ag-addition to Pb-doped Bi-system (Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_{2}Cu_{3}O_{5+x}wt\% Ag, with x varying from 0 to 50). These results are described in Chap.V. Unlike RE-based systems, here even small amount of Ag reduces the transition temperature of the compound. TEP behavior of silver added specimens also fits nicely the formula derived from marginal Fermi liquid hypothesis.

In Chap.VI, we take up the problem of percolation of thermoelectric power in inhomogeneous superconductors where one component is superconducting and the other nonsuperconducting. The motivation of this analysis comes from observations that for some oxygen deficient YBCO specimens TEP becomes zero at the temperature of the oxygen rich specimen, but the resistance remains finite, indicating that the fraction of superconducting phase is not large enough to percolate. Results discussed in Chap.IV and V for Sb and Li doped and Ag added specimens, show similar kind of paradoxical results as reported in Chap.I (sec.1.6), i.e., either a large difference in zero resistance temperature and zero TEP temperature or zero TEP with finite resistance. These results can be thought of in terms of lower percolation threshold for TEP as suggested by Jha et al. In this chapter first we analyse the simple argument of Jha et al that
even when the superconducting fraction is too low to percolate for conductivity there are paths along which the voltage drop due to temperature gradient is zero. We show that this argument can be cast in the form of a projected percolation, so that the zero voltage paths exist if the superconducting grains overlap in the direction of temperature gradient. This situation will lead to zero TEP but finite resistivity. We could show that the percolation threshold for TEP is zero in ideal situations but with large finite size corrections, which are quite important in a practical experimental situation. In order to further strengthen the conclusions reached on the basis of this percolation argument, we have calculated the TEP of random mixtures using effective medium approximation (EMA). We again find that if one of the components is superconducting, TEP will go to zero for any non-zero superconducting fraction.