CHAPTER IV

EFFECT OF SUBSTITUTIONS AT BI-SITE
4.1. INTRODUCTION

Substitution of small amount of Pb at Bi-site prompts the growth of 110K phase and renders stability to it (as has been already discussed in Chap. 3). There are several reports of still higher transition temperature for Bi-system with other dopants like Sb, Sn, Li etc. [1, 2]. Transition temperature of these materials changes either by a change in structure or/and by changing carrier concentration. Sb is one of the dopants which reportedly [2] increases the transition temperature to as high as 150K [2]. Sb and Bi are in the same group of the periodic table hence have the same valence state (3+, 5+). Sb is thus likely to replace at Bi-site. The ionic radius of Sb however being smaller than that of Bi, the substitution will change the structure. If Bi is replaced by any other element which is not in 3+, 5+ state, carrier concentration is likely to change. Ionic radii of alkaline metals is of the same range as the ionic radii of Bi, Pb, Sr, Ca and Cu (ionic radii of these are tabulated in table 4.1). These metals have +1 valence

\textbf{TABLE 4.1}

Ionic radii of different elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Valence State</th>
<th>Ionic Radius Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>+3</td>
<td>1.17</td>
</tr>
<tr>
<td>Sr</td>
<td>+2</td>
<td>1.40</td>
</tr>
<tr>
<td>Ca</td>
<td>+2</td>
<td>1.26</td>
</tr>
<tr>
<td>Cu</td>
<td>+2</td>
<td>0.71, 0.87</td>
</tr>
<tr>
<td>Li</td>
<td>+1</td>
<td>0.73, 0.90</td>
</tr>
<tr>
<td>Li-Cs</td>
<td>+1</td>
<td>0.73-1.81</td>
</tr>
</tbody>
</table>
state. Therefore doping by alkaline metals like Li is also an attractive and an interesting study to pursue. Since ionic radius of Li is much closer to Cu than that of Bi, substitution of Li at Cu-site is more probable. Li is however capable of occupying Bi, Sr and Cu sites [3], and substitution at Cu-site makes the best superconducting sample. Still we have substituted Li at Bi-site, just for comparing the results with Sb-substitution. In this chapter we discuss effects of Li and Sb doping on electrical resistance, thermoelectric power (TEP) and phase formatiôn. We also give theoretical description of TEP using marginal Fermi liquid (MFL) hypothesis.

Sb doping is reported to raise the transition temperature of Bi-system up to 150K with and without Pb [1]. Though such an effect seems to be transient, nevertheless to investigate this matter further we have studied the effect of Sb substitution for Pb in the BPSCCO system. Sb concentration (x) varies from 0 to 0.2 in Bi$_{1.6}$Pb$_{(0.4-x)}$Sb$_x$Sr$_{1.6}$Ca$_2$Cu$_{3}$O$_y$ specimens.

Effect of alkaline metals substitution has been studied in rare-earth based systems by Strobel et al [4], Ausloos et al [5], Suzeki et al [6]. Strobel et al reported a decrease in transition temperature with doping of Li but superconducting volume is more characteristic of a single phase. Effect of Li substitution has been studied by several groups, but the results are quite contradictory. We have studied the system
Bi_{1.6}Pb_{0.4-x}Li_{x}Sr_{1.6}Ca_{2}Cu_{3}O_{y}, with varying Li content (x) from 0 to 0.3.

4.2 EXPERIMENTAL: Samples are prepared by usual solid state reaction technique in two batches for Sb and Li doped specimens. Sb_{2}O_{5} and Li_{2}CO_{3} are used for Sb and Li doped specimens. Details are given in Chap.II (sec. 2.1.e).

Electrical resistance and thermoelectric power are measured by four probe technique and by differential method respectively as described in Chap.2. Room temperature XRD are recorded for the specimens in 2θ range of 3° to 45° using CuKα radiation. SEM micrographs have been taken on the fractured surface of the specimens doped with Li.

4.3 RESULTS AND DISCUSSION: The transition temperature (T_{c0}) is obtained by following the resistance of the specimens as shown in Fig. (4.1). Normalized resistance (R_{T}/R_{210}) vs. temperature curves are plotted for specimens Bi_{1.6}Pb_{0.4-x}Sb_{x}Sr_{1.6}Ca_{2}Cu_{3}O_{y} with values of x=0, 0.1, 0.2. Small concentration (0.1) of Sb increases the T_{c0} to 98K from 90K (T_{c0} of specimen without Sb), but further increase in Sb concentration reduces T_{c0} to a large extent (T_{c0} =84K for Sb=0.2). Normal state resistance shows a metallic behavior (dR/dT is positive), but metallicity (dR/dT) decreases with Sb-doping. Resistance for all the three specimens shows transition at 110K and finally drops to zero at T_{c0}. 104
For specimens with \( x=0 \) and 0.1 resistance shows only one broad drop but for \( x=0.2 \) resistance shows two drops at temperatures 110K and 100K. The onset temperature remains unchanged with Sb-doping without any signature of superconducting transition above 110K.

![Normalized resistance vs. temperature plots](image)

**Fig.4.1.** Normalized resistance vs. temperature plots for Sb doped specimens \( \text{Bi}_{1.6}\text{Pb}_{0.4-x}\text{Sb}_x\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_y \) \((x=0.0, \ 0.1 \ \text{and} \ 0.2)\).

**Fig.4.2** shows the normalized resistance \((R_T/R_{210})\) vs. temperature plots for Li doped specimen. As is evident from **Fig.4.2** that introduction of Li reduces the zero resistance temperature \((T_{c0})\) though the onset temperature is same (110K) for all the specimens. Small concentration of Li \((x=0.1)\) reduces
the $T_{c0}$ to 90K from the 98K (the $T_{c0}$ of specimen with $x=0$) Li=0.1 and 0.2 give the same resistance vs. temperature behaviour, whereas Li=0.3 results in a two step resistive transition corresponding to 110K and 80K phase with finite resistance down to 78K. By increasing Li content the transition width gets broadened and metallicity (dR/dT) decreases.

![Graph showing resistivity vs. temperature](image)

**Fig.4.2.** Normalized resistance vs. temperature plots for Li doped specimens $\text{Bi}_{1.6}\text{Pb}_{0.4-x}\text{Li}_x\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_y$ ($x=0.0, 0.1, 0.2$ and 0.3)

XRD spectra for the Sb-doped specimens show some very interesting results. For the specimen without Sb, XRD pattern shows only a high $T_c$ phase with some weak reflections corresponding to $\text{Ca}_2\text{PbO}_4$ and $\text{Ca}_2\text{CuO}_4$, the contribution from which
Fig. 4.3. Room temperature XRD pattern for Sb doped specimens in 2θ range of 3° to 45°. The appearance of a new phase (4441) at 2θ value between 29°-31° is noticeable.
seems to be very small. With small addition of Sb, the primary component corresponds to 2223 phase along with reflection from 2201 phase. Apart from the reflections already reported there are some extra peaks corresponding to 2θ values between 29°-31° with corresponding d' values of 2.988, 2.941 and 2.910 Å. These peaks have been reported by other groups also [7,8]. These peaks have been assigned to a Cu deficient phase with formula unit (BiSbPb)$_4$Sr$_4$Ca$_4$Cu$_4$O$_y$. Konstantinov et al [7] report this 4441 phase to be monoclinic which does not superconduct above $\text{LN}_2$ temperature, at the same time Xu et al [8] have reported this phase to be responsible for transition temperature higher than 110K. Further increase in Sb concentration ($x=0.2$) shows intense reflections for Ca$_2$PbO$_4$, 2201 phase and 4441 phase along with 2223 phase. The intensity of reflections corresponding to new phase has been increased to a large extent for $x=0.2$. XRD for all these specimens are shown in Fig.(4.3).

XRD and R-T for these specimens clearly show that Sb neither raises the $T_c$ of 2223 phase nor gives rise to the formation of any other new phase responsible for transition temperature higher than 110K. However, it leads to the formation of a new Cu-deficient phase, which is either non-superconducting or superconducting with a transition temperature lower than 110K. Doping with small concentration of Sb may stabilize the structure which in turn results in an increase in $T_c$. The reason for $T_c$ being low (90K) even for the specimen
without Sb may be that the superconducting grains are not well connected, as the specimen preparation lacks the intermediate grinding.

Room temperature XRD for the Li-doped specimens are shown in Fig. 4.4. Specimen without Li shows reflections corresponding to 2223 phase only. Li addition leads to formation of 2212 phase, 2201 phase with some other impurities like Ca$_2$ PbO$_4$ and CuO. Intensities for these reflections increase with increasing Li-content. Appearance of CuO peaks with Li doping is similar to reports of Kawai et al [3], but they have reported an increase of $T_c$ for 2212 phase, which is contradictory to our observation of a decrease of $T_c$. Whether the increase of Li-content or the decrease in Pb content results in this kind of behaviour is not very clear from these studies. Li concentration of 0.3 would correspond to Pb concentration of 0.1, and that low concentration of Pb itself is responsible for two step incomplete transition. As has been in the studies of Kawai et al [3] and Matsubara et al [9] that transition temperature increases with the Li incorporation, is not seen here. Our results suggest that Li does not raise transition temperature of either phase (2212 or 2223).

SEM (scanning electron microscope) photographs for the Li-doped specimens are shown in Fig. 4.5. For specimen without Li ($x=0$) grains are platelet-like (elongated), which corresponds
Fig. 4.4. Room temperature XRD patterns for Li doped specimens in 2θ range of 3° to 45°.
Fig. 4.5 SEM micrographs for Li-doped specimens with concentrations 0.0, 0.2 and 0.3.
to 110K phase. Specimen with Li=0.2 shows some round shaped grains along with platelet like grains, indicating the presence of some more phase/phases other than the 110K phase. Further increase in Li concentration shows predominance of other phases on the 110K phase as the density of elongated grains has been reduced. SEM supports that the Li addition leads to the decomposition of 110K phase in to 2212 phase and 2201 phase along with some impurities.

TEP for all the specimens with varying Sb content is also positive (Fig.4.6) in the temperature range covered (i.e. 80K to 300K). All the specimens show maxima in thermoelectric power in the temperature range 111-125K with maximum values ($S_m$) varying between 19.4μV/K (for Sb=0) to 11.6μV/K (for Sb=0.2).
TEP goes to zero at 98K for all the specimens and remains so below this temperature ($T_{s0}$) due to onset of superconductivity. Above maxima it decreases linearly with temperature.

TEP for the Li doped specimens with Li content as 0, 0.2 and 0.3 are shown in Fig.4.7. TEP for all the specimens is positive in the temperature range covered. There appears a peak in TEP vs. temperature plots at temperatures ($T_n$) 115K, 127K and 137K for $x=0$, 0.2 and 0.3 respectively. Above this maxima TEP decreases with increasing temperature and below this maxima it goes to zero at a temperature ($T_{s0}$) depending on the value of $x$; 101K for $x=0$ and 95K for $x=0.2$ and 0.3. Maximum value of thermoelectric power ($S_n$) decreases with increase in Li content. TEP behaviour is very similar to the behaviour reported in chapter 3.
Zero resistance temperature ($T_{c0}$), zero TEP temperature ($T_{s0}$), maximum value of TEP ($S_m$) and the temperature where maxima appears in TEP ($T_m$) are summarized in Table 4.2 for all the specimens.

**TABLE 4.2**

Maximum Value of TEP ($S_m$), TEP peak temperature ($T_m$), zero TEP temperature ($T_{s0}$) and zero resistance temperature ($T_{c0}$) for Sb and Li doped specimens.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$S_m$ (μV/K)</th>
<th>$T_m$ (K)</th>
<th>$T_{s0}$ (K)</th>
<th>$T_{c0}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bi$<em>{1.6}$Pb$</em>{0.4}$-xSb$<em>x$Sr$</em>{1.6}$Ca$_2$Cu$_3$O$_y$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=0.0</td>
<td>19.4</td>
<td>120</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>x=0.1</td>
<td>16.4</td>
<td>120</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>x=0.2</td>
<td>11.6</td>
<td>115</td>
<td>98</td>
<td>84</td>
</tr>
<tr>
<td>2. Bi$<em>{1.6}$Pb$</em>{0.4}$-xLi$<em>x$Sr$</em>{1.6}$Ca$_2$Cu$_3$O$_y$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=0.0</td>
<td>14.4</td>
<td>120</td>
<td>101</td>
<td>98</td>
</tr>
<tr>
<td>x=0.2</td>
<td>13.0</td>
<td>127</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>x=0.3</td>
<td>11.0</td>
<td>137</td>
<td>95</td>
<td>**</td>
</tr>
</tbody>
</table>

** Resistance is finite down to 77K.

4.3.a. **THEORY:** The thermoelectric power $S$ consists of two components namely, diffusion component $S_d$ and phonon-drag component $S_q$. According to elementary theory of degenerate free electron gas [10]

$$S_d = \pi^2 k_B^2 T / 3e \epsilon_F$$  \hspace{1cm} (4.1)

and

$$S_q = C / 3n \epsilon_r$$  \hspace{1cm} (4.2)

where $e$ is the charge of the carrier, $\epsilon_r$ the fermi energy, $n$
the electron density and $C_q$ the lattice specific heat. At low temperatures $S_q$ varies as $T^3$ and at high temperatures as $1/T$. According to simple metallic theory $TEP$ can be expressed as

$$ S = AT + \frac{B}{T} \quad (4.3) $$

where $A$ gives the diffusion component of $TEP$ and $B$ the phonon-drag component. The sign of $A$ generally is the sign of charge carriers (as discussed in Chap.1). If one tries to fit the $TEP$ data of high temperature oxide superconductors to the above expression one usually finds a negative diffusion component and a very large phonon drag contribution. Whereas the Hall coefficient is positive indicating the charge carriers are holes, moreover such kind of fits show deviations from the formula at low temperatures (below 160K). This deviation has been attributed to superconducting fluctuation effects by Kumar [11]. Because of short coherence length and two dimensional nature of these oxides, fluctuations can be effective at temperatures as high as 150K. The expression for $TEP$ including the fluctuation factor is given as [11],

$$ S_F(T) = S_B(T) \frac{1}{1 + \frac{\gamma}{\ln |\frac{T}{T - T_c}|}} \quad (4.4) $$

where $\gamma$ is a constant, $T_c$ is the transition temperature, $S_F(T)$ is $TEP$ at temperature $T$ and $S_B(T)$ is bare $TEP$ at temperature $T$.
obtained using simple metallic theory. Using this formula TEP can be explained for pure systems as shown in Fig.4.8, but for doped specimens it shows some deviations at low temperature (≈150K).

![Diagram](image)

**Fig.4.8.** Experimentally measured TEP plotted against temperature for pure specimen along with values of TEP obtained from Eq.4.3 and Eq.4.4.

Marginal Fermi liquid hypothesis has been used to explain a number of properties of these superconductors [12]. So we have tried to understand TEP of these materials in the higher temperature range (130K to 300K) in the same spirit [13]. The marginal fermi liquid hypothesis consists in assuming the following form for the self energy $\Sigma(k,c)$ of charge carriers,

$$
\Sigma(k,c) = \lambda \left[ \epsilon \ln \frac{x}{\hbar \omega_c} - i \frac{\pi}{2} x \right] \tag{4.5.a}
$$

$$
x = \max \left( |c|, \frac{k_B T}{116} \right) \tag{4.5.b}
$$
where \( \lambda \) is a dimensionless coupling constant and \( \hbar \omega_c \) is a cut-off frequency such that the above expression is valid only for \( \varepsilon < \hbar \omega_c \). Using this self energy, electrical conductivity and TEP are obtained in the following form [13]

\[
\sigma = \frac{n e^2 h}{m^* \pi \lambda k_B T} \quad (4.6)
\]

and

\[
S_d = \frac{\pi^2}{2} \left( \frac{k_B}{e} \right) \left( \frac{k_B T}{e_F} \right) \left[ 1 - \frac{k_B T}{\hbar \omega_c} \right] \quad (4.7)
\]

Eq.4.7 is only the diffusive part of thermoelectric power. If we take the Debye temperature of the material to be 400K, for the temperature range of interest we can use the high temperature form of the phonon-drag term, to incorporate it as

\[
S = S_d + \frac{B}{T} \quad (4.8)
\]

where \( B \) is to be determined empirically. Note that unlike other formulae [14, 15] for high temperature behaviour of \( S_d \), Eq.4.7 has the correct behaviour in the \( T \rightarrow 0 \) limit.

4.3.b. COMPARISON WITH THEORY: In order to compare the experimental data with the formula derived in Eq.4.7, we first make a plot of \((S/T)^{1/2}\) vs. \( \ln T \), which should be a straight line
according to Eq.(4.7). These plots for several systems in the temperature range of 120K to 300K are shown in Fig.4.9 and are seen to be nice straight lines. These fits are much better than the fits to conventional formula that we tried (e.g. \( S = AT + \frac{B}{T} \)).

![Graph showing (S/T)^1/2 vs. LnT plots for different concentration of Sb and Li.](image)

**Fig.4.9.** \((S/T)^{1/2}\) vs. \(\text{LnT}\) plots for different concentration of Sb and Li.

This also means that the phonon-drag term is somehow quite small. We shall discuss this point a little later. In order to achieve quantitative comparisons and obtain values of parameters involved in MFL hypothesis, we need to fix some basic parameters. For this, we derive partial information from the
conductivity formula i.e. Eq.4.6, which yields the linear slope of resistivity \((d\rho/dT)\) to be

\[
\frac{d\rho}{dT} = \frac{m^*\pi k_B \lambda}{ne^2\hbar}
\]  

(4.9)

Now approximately for our specimens the average value of \((d\rho/dT)\) is \(1\times10^{-7}\Omega\text{m}/\text{K}\). This is also the order of magnitude for other measurements reported in literature. Note that the slope of straight lines in Fig.4.9, is \(-\lambda(\pi^2k_B^2/2e\xi)\)\(^{1/2}\) and its intercept on vertical axis is \((\pi^2k_B^2/2e\xi)\)\(^{1/2}\) \([1+i\ln(h\omega_c/k_B)]\).

Thus if we fix \(n\) and \(m^*\), we should be able to obtain parameters \(\lambda\), \(h\omega_c\) and \(\xi\). We have taken \(n=3\times10^{21}/\text{cc}\) for pure Bi-system, which is roughly the hole density obtained by assuming one hole per unit cell. We take \(m^*\) to be five times the electron mass. Eq.4.8 then yields \(\lambda=4\) (Table 4.3 give value for all the specimens).

Now the slopes and intercepts of straight lines like that of Fig.4.9 are used to determine \(\xi\) and \(h\omega_c\). However, these parameters do not enable us to fit the experimental data well. Better fits are obtained for values of \(\xi\) and \(h\omega_c\) which are about 15 to 25% higher. The simplest way to resolve this discrepancy is to attribute it to vertex correction factor \(\gamma\) which is present in the formula for conductivity but cancels out (in this simple theory) from the formula for thermoelectric
power. The values of \( \varepsilon_r \) fitting the data best for thermoelectric power are listed in Table 4.3. The values of \( \hbar \omega_c \) obtained by a combination of fitting the y-axis intercept in Fig.4.9 and actual fitting with the data are found to be of order 300K.

**TABLE 4.3**

Value of coupling constant (\( \lambda \)), estimated Fermi energy (\( \varepsilon_F \)), Cut-off frequency (\( \hbar \omega_c \)) and value of Phonon drag component (\( B \)) are tabulated for Sb and Li doped specimens \([\text{Bi}_{1.6}\text{Pb}_{0.4-x}\text{M}_x\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_{y}]\), where \( M=\text{Sb} \) or \( \text{Li} \). The two values of Fermi energy correspond to \( B=0 \) and \( B\neq0 \).

<table>
<thead>
<tr>
<th>Compositions</th>
<th>( \lambda )</th>
<th>( \varepsilon_F(K)(B=0) )</th>
<th>( \hbar \omega_c(K) )</th>
<th>( B(\mu\text{V}) )</th>
<th>( \varepsilon_F(K)(B\neq0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( M=\text{Sb} )</td>
<td>x=0.0</td>
<td>4</td>
<td>51000</td>
<td>300</td>
<td>-150</td>
</tr>
<tr>
<td></td>
<td>x=0.1</td>
<td>4</td>
<td>78000</td>
<td>300</td>
<td>-140</td>
</tr>
<tr>
<td></td>
<td>x=0.2</td>
<td>4</td>
<td>99000</td>
<td>300</td>
<td>-120</td>
</tr>
<tr>
<td>2. ( M=\text{Li} )</td>
<td>x=0.0</td>
<td>4</td>
<td>65000</td>
<td>300</td>
<td>-100</td>
</tr>
<tr>
<td></td>
<td>x=0.2</td>
<td>4</td>
<td>70000</td>
<td>300</td>
<td>-80</td>
</tr>
<tr>
<td></td>
<td>x=0.3</td>
<td>4</td>
<td>90000</td>
<td>300</td>
<td>-60</td>
</tr>
</tbody>
</table>

Next we come to the consideration of phonon-drag effect. As remarked earlier, the formulae 4.7 and 4.8 suggest a rather small effect. Since the MFL hypothesis implies a lack of well-defined quasi-particles, the form of phonon-drag term may be quite different and its magnitude much smaller than that in conventional system. In any event, when we fit the data according to Eq.4.8, we find that reasonably good fits are obtained by taking \( B \) to be negative and of order 100 to 150\( \mu \text{V} \). This value of \( B \) is one order of magnitude smaller than what
would be obtained in conventional fittings done according to Eq. 4.1 and 4.2. The values of B are also listed in Table 4.3.

![Diagram](image)

**Fig. 4.10.** Theoretical values of TEP for Sb and Li doped specimens calculated from the values of parameters given in Table 4.3, along with the measured TEP. Dashed line represents the plots for $S_d$ and solid lines for $S_d + \frac{B}{T}$.

Another noteworthy feature of this fitting is that the values of parameters vary rather systematically with dopant concentration. $\varepsilon_f$ seems to be increasing linearly with both Li and Sb doping, however this may not quite reflect the correct situation, as the value of carrier concentration has been kept fixed throughout these fittings.
The observed difference in $T_{c_0}$ and $T_{s_0}$ is an exciting and surprising result. This difference is similar to that earlier observed by Grant et al [16] in La-system, Jha et al for Y-system [17] and Bi-system [18] and by Yan et al [19] for Y-system. This point will be discussed in detail in Chap.VI using some theoretical calculations to show that the percolation threshold for TEP is indeed smaller than the usual percolation threshold for conduction. That's why we could observe zero TEP for Li concentration of 0.3 at 95K though the resistance is finite down to 77K; and $T_{s_0}$ to be of 98K for all the Sb doped specimens even though $T_{c_0}$ is reduced by Sb-doping.

4.4. CONCLUSIONS: From the results discussed in this chapter following conclusions can be drawn:

(i) Small concentration of Sb (0.1) to BPSCCO compound increases $T_{c_0}$ whereas further increase in Sb concentration (0.2) decreases $T_{c_0}$ drastically,

(ii) Sb doping results in formation of a new phase (4441), corresponding d values for this new phase are 2.988, 2.941 and 2.910 Å.

(iii) Li doping decreases $T_{c_0}$ of the Pb doped BSCCO compound, even small concentration of Li induces some impurity like CuO and Ca$_2$CuO$_4$.

(iv) TEP can be well fitted to the expression obtained using MFL hypothesis.
REFERENCES


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