Chapter 3

Influence of Pb on the transport properties of Bi-2212

_Everything should be made as simple as possible, but not simpler._
— Albert Einstein, 1879–1955

3.1 Introduction

Superconductivity in the high $T_c$ superconducting cuprates (HTSCs) is two dimensional. This is partly caused by the characteristic crystal structure consisting of alternate stacks of superconducting CuO$_2$ planes and insulating reservoir blocks along the c-axis. In the superconducting state, carriers move in the c-direction by tunnelling the blocking layers via the Josephson interlayer coupling and hence, the superconducting properties of HTSC are strongly affected by the strength of this coupling. In the case of Bi-based superconductors, most of the H-T vortex phase diagram is dominated by the presence of the vortex liquid phase. This is due to the large anisotropy, which is responsible for weak inter-layer two dimensional pancake vortex coupling [1]. Bi-based
superconductors are the most anisotropic HTSC compounds due to the thick blocking layers consisting of insulating Bi-O double layers.

Among the Bi-based superconductors, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) system has always been a material of interest for both technologists and theorists. This is because the doping studies on these materials were helpful to improve many properties of the system such as critical temperature $T_c$, critical current density $J_c$, magnetic behaviour and thereby exploiting the material for practical applications. Besides these, its thermodynamic and structural stability is relatively invariant against large variations in the processing conditions or different cationic substitutions. Doping in Bi-2212 superconductor generally involves adding impurities or charge carriers into the inert parent material by chemical substitution or addition or removal of oxygen atoms from the charge reservoir planes. Doping an impurity atom in Bi-2212 system strongly perturbs the surrounding electronic environment and can therefore be used as a powerful tool to probe the HTSC at atomic scale and hence can explore its fundamental mechanism and occurrence.

This chapter describes the influence of Bi:Pb ratio on the structural and superconducting properties of: 1. (Bi,Pb)-2212 superconductor and 2. (Bi,Pb)-2212 doped with a typical rare earth, Yttrium. Y is used for the investigation because of the comparable ionic radii and the ability to contribute more electrons to the crystal lattice. The solid state route is chosen for the preparation of Bi-2212 superconductor, since it is an easier and scalable method for large scale production.

The detailed analysis of the results on the substitution of Pb at Bi-site of Bi-2212 revealed that the Pb doped Bi-2212 has much superior transport properties than undoped Bi-2212, even though, a slight reduction in the $T_c$ was observed. The range of Pb substitution for achieving the best superconducting properties for Bi-2212 was found to be within $x = 0.4 - 0.5$. Hence, during Y doping in Bi-2212, the Pb content was fixed as $x = 0.4$. The results of this study
show that $T_c$ and $J_c$ are significantly enhanced for optimum Y concentration in Pb doped Bi-2212. These variations in the electrical and superconducting properties of Y doped (Bi,Pb)-2212 were the consequences of the structural and electronic changes due to Pb and Y co-doping.

### 3.2 Experimental

Pb-doped Bi-2212 superconductor was prepared by conventional solid state diffusion method. The initial stoichiometry of $\text{Bi}_{(2,1-x)}\text{Pb}_x\text{Sr}_2\text{Ca}_{1.1}\text{Cu}_{2.1}\text{O}_{8+\delta}$ was chosen such that $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 and the corresponding samples were labelled as Pbo, Pb1, Pb2, Pb3, Pb4 and Pb5, respectively. High purity carbonates and oxides (Aldrich, > 99.9 %) were weighed using an electronic balance (*Mettler AE240*) and thoroughly homogenized using a planetary ball mill (*Fritsch pulverisette 6*) with agate bowl and balls in acetone medium for 1 hour. The samples were subjected to a three stage calcination process in air at a heating rate of 2 °C/min at 800 °C/15h, 820 °C/25h and 830 °C/40h, respectively, with intermediate grinding in acetone medium. Circular pellets of the samples with dimensions of ~ 12 mm diameter and ~ 1 mm thickness were prepared using a cylindrical die under a pressure of 600 MPa in a hydraulic press (Herzog 12 TP). These pellets underwent a two stage heat treatment (845 °C/60h + 848 °C/60h) with one intermediate uniaxial pressing at the same pressure.

Yttrium added (Bi,Pb)-2212 superconductor with a general stoichiometry of $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{2.0}\text{Ca}_{1.1}\text{Cu}_{2.1}\text{Y}_{x}\text{O}_{8+\delta}$ (where $x = 0$ to 0.5) was prepared by the same method as described above using high purity carbonates and oxides of the ingredients (Aldrich, > 99.9 %). The Y added (Bi,Pb)-2212 samples are labelled hereafter as Y0, Y1, Y2, Y3, Y4 and Y5, respectively, for $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5.
Phase analysis of the calcined powder and sintered samples were done by a powder X-ray diffractometer (*Philips X’pert Pro*) equipped with an *X’celerator* and a monochromator at the diffraction beam side, using *CuKα* radiation to monitor the crystal structure, grain orientation and phase assemblage. *X’Pert Highscore* software was used for the phase identification with the help of *ICDD PDF2* database. Microstructural analysis of the samples were done using scanning electron microscopy (*JEOL JSM 5600LV*) and elemental analyses of the samples were done using energy dispersive X-ray spectrometer (*Phoenix*) equipped with SEM. Density of the samples were determined by measuring their mass and the dimensions. Electrical contacts were made using conducting silver paste, coated prior to the sintering stage and co-fired with the pellets. The transition temperature (*Tc*) of the samples were determined by R-T measurement using four-probe DC electrical resistance method. The transport critical current density (*Jc*) measurements were performed using standard four-probe technique adopting the $1\mu V/cm$ criterion at 64 K in an indigenously built vacuum bath cryostat.

### 3.3 Effect of Bi:Pb ratio on the superconductivity of (Bi,Pb)-2212

#### 3.3.1 Introduction

Several investigations have pointed out that Pb substitution in Bi-2212 [2-6] affects the structural modulation and the characteristic incommensurate modulation increases [5,6]. Studies on single crystals reported that Pb at the Bi-site hinders the insertion of additional oxygen atoms into Bi-O double layers [6]. The substitution of Pb accompanied by removal of oxygen atoms in the Bi-O layers leads to infinite structural modulation (no modulation). As a result, the anisotropy of modulation free crystals is strongly reduced [7]. The
but-of-plane resistivity decreases by four orders of magnitude in Pb-doped crystals [8]. Motohashi et. al have found from the in-plane ($\rho_a$ and $\rho_b$) and out-of-plane ($\rho_c$) resistivity measurements that the anisotropy of Bi-2212 single crystals in the normal state is drastically reduced by Pb doping [9, 10].

But most of these results were obtained from single crystals which cannot be used for producing composite polycrystalline conductors for practical applications. Moreover, the maximum current carrying capacity of these materials were estimated by the magnetisation measurements, where the supercurrents induced by magnetic field can only flow through the areas with good conductivity and were less influenced by the extrinsic factors, such as impurity phases, non-uniformity in oxide layer thickness and damage in oxide layers. But in a practical case, these extrinsic factors can not be neglected. Thus, the transport current measurements in polycrystalline samples are necessary for a better understanding of the relationship between the microstructure and current carrying properties of Bi-2212 for practical applications. This section describes the effect of substitution of varying amounts of Pb in Bi-site on the transport properties of polycrystalline Bi-2212.

### 3.3.2 Result and Discussion

Figure 3.1 shows the XRD patterns of Bi$_{(2,1-x)}$Pb$_x$Sr$_2$Ca$_{1.1}$Cu$_{2.1}$O$_{8+\delta}$ samples (where $x = 0.0$ to 0.5) after the second stage calcination at 820 °C for 25 hours (Sample preparation is described under section 3.2). X-ray analysis of the calcined powder indicates that both the Pb-free and the Pb substituted samples consist of multiphases and their diffraction patterns contain peaks of Bi-2212 as the major phase. Minor phases, namely Bi-2201 and Ca$_2$PbO$_4$ are present in all the doped samples. In the case of undoped sample, Bi-2201 is the only secondary phase. The volume fraction of different phases such as Bi-2212/(Bi,Pb)-2212, Bi-2201 and Ca$_2$PbO$_4$ are estimated by measuring the integrated peak intensities of all the major XRD peaks of the respective phases.
Figure 3.1: XRD patterns of the samples after calcination at 820 °C / 25 h.

Figure 3.2: XRD patterns of the samples after final stage sintering at 848 °C / 60 h.

using the formula $F_x = \left( \frac{\sum I_x}{\sum I} \times 100 \right)$ where, $x$ is any phase. $F_x$ is the volume percentage of phase $x$, $I_x$ is the integrated peak intensities of phase $x$ and $I$
is the integrated peak intensities of all the phases present in the sample. The estimated phase assemblage is given in Table 3.1. It can be seen that the Pb-free sample, Pb0 consists of a considerable amount of Bi-2201 (36.3 %) and the phase remaining is Bi-2212 (63.7 %). No other secondary phases were observed in this sample. In the Pb-doped samples, the volume percentage of \((\text{Bi,Pb})\)-2212 increases with the amount of Pb content up to Pb5 sample (94.8 %). The fraction of Bi-2201 decreases considerably to 3.4 %, while that of \(\text{Ca}_2\text{PbO}_4\) increases to 1.8 % for Pb5 sample (Table 3.1). This shows that the reaction kinetics become faster for the Pb-doped samples compared to the undoped sample. The very low fraction of \(\text{Ca}_2\text{PbO}_4\), the only secondary phase containing Pb in the system, indicates that most of the added Pb gets fixed to Bi-2212 and forms \((\text{Bi,Pb})\)-2212.

Figure 3.2 shows the XRD patterns of the samples after the final stage of sintering at 848 °C. The patterns reveal the presence of Bi-2212/(\text{Bi,Pb})-2212 only and no peaks of any secondary phases containing Pb or any other cations is observed even up to Pb5. This shows that Pb atoms are incorporated into the lattice site of the crystal structure of Bi-2212 up to the solubility limit of Pb at \(x \leq 0.5\). Lotgering index \((F)\), a measure of texture [12, 13] of the grains of undoped and Pb substituted samples was calculated from the XRD patterns of the sintered pellets and their ground powders (Table 3.2). It shows that the texture of the samples systematically improves with increasing Pb content in Bi-2212. The Pb5 sample has the highest value of Lotgering index \((F_{\text{max}} = 0.85)\), while the sample Pb0 has a \(F\) value of 0.76.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Pb0</th>
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<th>Pb2</th>
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<td>(Vol %)</td>
<td>(Vol %)</td>
<td>(Vol %)</td>
<td>(Vol %)</td>
<td>(Vol %)</td>
<td>(Vol %)</td>
</tr>
<tr>
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<td>83.1</td>
<td>86.5</td>
<td>90.5</td>
<td>94.8</td>
</tr>
<tr>
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<td>20.4</td>
<td>15.8</td>
<td>12.2</td>
<td>7.9</td>
<td>3.4</td>
</tr>
<tr>
<td>(\text{Ca}_2\text{PbO}_4)</td>
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<td>1.1</td>
<td>1.3</td>
<td>1.6</td>
<td>1.8</td>
</tr>
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</table>

Table 3.1: Phase assemblage of undoped and Pb substituted Bi-2212 samples.
Figure 3.3: Variation of lattice parameters as a function of Pb substitution.

The lattice parameters of the samples calculated from the XRD patterns of the final samples are shown in figure 3.3. The formula, 

\[ \frac{1}{d^2} = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) \]

is used for the calculation, which is based on an orthorhombic symmetry assumed for (Bi,Pb)-2212. No appreciable change in lattice parameters is observed with Pb-doping. The a and b lattice parameters increase slightly from 5.398 and 5.402 to 5.404 and 5.406, respectively, starting from Pb0 to Pb5. The variation of c lattice parameter is still insignificant. But the formed (Bi,Pb)-2212 system retains its orthorhombic symmetry up to the doping level of \( x = 0.5 \). These observations show that the replacement of Bi atoms with Pb atoms does not affect the crystal structure of Bi-2212 appreciably because of the comparable ionic radii of Bi\(^{3+} \) (1.03 Å) and Pb\(^{2+} \) (0.98 Å) ions.

Figure 3.4 shows the SEM micrographs of the fractured surfaces of the samples. The microstructure of the samples seems to improve with the increase in Pb content. Flaky grains with the layered morphology, typical of Bi-2212 are observed in all the samples. Considering the texturing or grain alignment and densification of samples, Pb5 shows the best microstructure among all the
Figure 3.4: SEM micrographs of the fractured surface of undoped and Pb substituted samples taken in secondary electron imaging mode.

Figure 3.5: Density variation of the samples after different stages of heat treatment.
samples. This is also seen in the density variation of Pb-substituted samples (Figure 3.5). Figure 3.5 shows the variation of the bulk density of the samples at different stages of heat treatment with respect to the Pb content and the obtained density as compared to the theoretical density of Bi-2212 ($\rho_{th} = 6.6 \text{ g/cm}^3$). The sintered density of all the samples after the first stage sintering are less by $\sim 10\%$ than that of the corresponding green density (density of pellets prior to the heat treatment). The deterioration of sintered density, usually referred to as the retrograde densification, is a characteristic property of (Bi,Pb)-2212 due to its layered growth mechanism [14–16]. The undoped sample (Pb0) shows a lower bulk density than the Pb substituted samples at this stage. The density of all the samples is improved significantly by the intermediate pressing. The highest and lowest bulk densities are shown by Pb5 (5.64 g/cm$^3$) and Pb0 (5.40 g/cm$^3$) samples, respectively.

Figure 3.6 shows the temperature dependence of resistivity of undoped and Pb substituted samples ($0.0 \leq x \leq 0.5$). All the samples show superconductive transition. A pseudo-transition occurs around $\sim 110 \text{ K}$ as indicated by a slight drop in resistance for samples with $x = 0.1$ to 0.4, which is due to the

<table>
<thead>
<tr>
<th>Pb content $(x)$</th>
<th>$\Delta T_c$ (K)</th>
<th>Lotgering index $(F)$</th>
<th>$J_c$ at 64 K (A/cm$^2$)</th>
<th>$\alpha(T) \times 10^{-4}$/K</th>
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<tr>
<td>0.5</td>
<td>4.40</td>
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</table>

Table 3.2: Transition width ($\Delta T_c$), Lotgering index $(F)$, Self field $J_c$ at 64 K and temperature coefficient of resistance [$\alpha(T)$] at normal state of undoped and Pb substituted Bi-2212 samples.
Figure 3.6: Temperature dependent normalized resistivity plots of Pb substituted samples.
co-existence of the triple layered cuprate (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ [(Bi,Pb)-2223] in very low percentages which could not be detected within the detection
limit of the X-ray diffractometer, while Pb0 and Pb5 samples do not show this anomaly. Figure 3.7 shows the variation of critical temperature ($T_c$) and critical current density ($J_c$) as a function of Pb content of superconducting samples. The critical temperature as determined from the $\rho$-$T$ plots shows that the $T_c$ of the Pb substituted samples slightly decreases with Pb content. Lowest $T_c$ is shown by Pb4 sample (76.8 K) while the highest $T_c$ is shown by Pb0 (81.3 K). The values of transition width ($\Delta T_c$) are also found to be almost same for Pb substituted samples but these are slightly higher than that of the undoped Bi-2212 (Table 3.2). The results reveal that the substitution of Pb$^{+2}$ ion for a Bi$^{+3}$ increases the hole concentration of the Bi-2212, which in turn reduces the $T_c$ of Pb substituted Bi-2212 superconductor.

Figure 3.7 also shows that as Pb content increases, $J_c$ value increases, and reaches to a maximum for Pb5 (120 A/cm$^2$) at 64 K as against 48 A/cm$^2$ for the pure sample. It is also observed that the rate of increase in $J_c$ at around $x = 0.4 - 0.5$ is significantly reduced. Figure 3.8 shows the variation of normal state resistivity and residual resistivity ratio (RRR) of undoped and Pb-doped Bi-2212 superconductor. It is found that the normal state resistivity of the samples rapidly decreases with Pb content, while the residual resistivity ratio (RRR) increases up to $x = 0.5$. The temperature coefficient of resistance [$\alpha(T)$], also shows an increasing trend with Pb content (Table 3.2). This implies that the charge carriers in the system increases and the normal state resistivity of the Pb substituted samples get reduced. The improvement in $J_c$ of Pb substituted Bi-2212 is due to the improvement in microstructure and the conductivity along the c-axis which strengthen the Josephson's coupling.

The XRD profile and the lattice parameter results show that the Pb atoms are successfully substituted for Bi-site in Bi-2212 as envisaged in the nominal stoichiometry. Substitution of Pb leads to the replacement of Pb$^{+2}$ by Bi$^{+3}$ ions and this decreases the oxygen content. The introduced divalent Pb ions lead to lesser oxygen content in Bi-O layer which yield a longer periodicity of modulation. The substitution also increases the hole concentration.
on the CuO$_2$ layers. This explains the slight decrease in $T_c$ with Pb substitution. The effect of slight reduction of $T_c$ is not reflected in the observed $J_c$ of Pb substituted samples because of the better microstructural properties and c-axis conductivity of these samples. The Pb-doping reduces the weak-links between the grains which enables a resistance free current distribution in (Bi,Pb)-2212 superconductor. This also contributes to the effective normal state resistivity as compared to undoped Bi-2212, hence further improving the $J_c$ of Pb-substituted (Bi,Pb)-2212 superconductor.

3.4 Effect of Bi:Pb ratio on the superconductivity of RE-doped (Bi,Pb)-2212

3.4.1 Introduction

Cationic substitution of a trivalent Rare Earth (RE) element in the place of a divalent Ca$^{+2}$/Sr$^{+2}$ ion, induces variation in hole concentration of the CuO$_2$ planes in the Bi-2212 superconductors [17–21]. Thus, by tuning the level of the substitution, an optimum carrier concentration can be achieved which will enhance the critical temperature ($T_c$) of the system [22].

Extensive studies on RE substitution in Bi-2212 have been performed of which majority of studies were done on the substitution of Yttrium (Y) at Ca site [17–21, 23–39] because of their comparable ionic size. A few studies were done at the Sr and Bi-sites also [40, 41]. All these studies were done on the general formula of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ which is a Pb-free system. Also, in the previous section, it is experimentally verified that Pb substitution at Bi-site in Bi-2212 significantly improves the c-axis conductivity and thereby improves the coupling between the CuO$_2$ layers. Thus it is expected that the combined effect of Pb doping at Bi-site associated with RE addition in Bi-2212
can enhance the superconducting properties of the system significantly. In the present section, the enhancement of $T_c$ and self-field $J_c$ of Y added Bi-2212 superconductor co-doped with Pb at Bi-site is discussed.

### 3.4.2 Results and Discussion

Figure 3.9 shows the XRD patterns of Bi$_{1.7}$Pb$_{0.4}$Sr$_{2.0}$Ca$_{1.1}$Cu$_{2.1}$Y$_x$O$_{8+\delta}$ (where $x = 0$ to 0.5) samples after the second stage calcination at 820 °C for 25 h (Sample preparation is described under section 3.2). X-ray analysis indicates that all the samples contain peaks of (Bi,Pb)-2212 as the major phase and Bi-2201, Ca$_2$PbO$_4$ and Sr$_2$PbO$_4$ as minor phases. The volume fraction of different phases such as (Bi,Pb)-2212, Bi-2201, Ca$_2$PbO$_4$ and Sr$_2$PbO$_4$ were estimated and it can be seen that the volume percentage of (Bi,Pb)-2212 remains almost same up to Y2 sample (94.1 %) and thereafter it decreases to 91.8 % for Y5 ($x = 0.5$) (Table 3.3). In sample Y5, small amounts of Sr$_2$PbO$_4$ is also detected as the secondary phase. This shows that at lower Y stoichiometry replacement of Ca$^{+2}$ by Y$^{+3}$ takes place, but at higher Y stoichiometry replacement of Sr$^{+2}$ by Y$^{+3}$ also takes place resulting in the precipitation of Sr$_2$PbO$_4$. Figure 3.10 shows the XRD patterns of the samples after final stage of sintering. The XRD profile indicates that the only phase detected is (Bi,Pb)-2212 and no peaks of any secondary phases are detected up to Y5. This indicates that the solubility limit of Y in the system is $x \leq 0.5$ and the added Y enters into the crystal structure in all the Y doped samples [42]. Lotgering index ($F$) calculated from the XRD patterns (Table 3.4) shows that the grain orientation gradually comes down as the Y content increases. The pure sample shows the highest value of Lotgering index ($F_{max} = 0.75$), while the sample Y5 shows a $F$ value of 0.41.

Figure 3.11 shows the variation of the bulk density of the samples at different stages of the processing schedule. The measured density as compared to the theoretical density of Bi-2212 ($\rho_{th} = 6.6$ g/cm$^3$) in percentage is given in
Figure 3.11. The sintered density of all the samples after the first stage sintering are less by \( \sim 6\% \) than that of the corresponding green density. The sintered density has been improved by the intermediate press-sintering step. Densities of all the Y added samples are less than the pure sample \((5.54 \text{ g/cm}^3)\) and the

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**Figure 3.9:** XRD patterns of the samples after calcination at \(820^\circ\text{C} / 25\ h\).

**Figure 3.10:** XRD patterns of the samples after final stage sintering at \(848^\circ\text{C} / 60\ h\).
decrease is found to be a function of Y content. The minimum density was obtained for Y5 (4.99 g/cm$^3$).

Figure 3.12 shows the SEM microstructure of the samples taken in the SEI mode. The morphology of the grains show a vivid variation with increase in Y content. Characteristic flaky grains of (Bi,Pb)-2212 are seen in all the samples. Clean, large and oriented grains are the identity of Y0 and Y1 samples. As Y level increases, the porosity of the samples increases with deterioration in the

<table>
<thead>
<tr>
<th>Phase</th>
<th>Y0</th>
<th>Y1</th>
<th>Y2</th>
<th>Y3</th>
<th>Y4</th>
<th>Y5</th>
</tr>
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</tr>
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</tr>
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</table>
size and orientation of grains for samples ranging from $0.2 \leq x \leq 0.5$. Thus, the decrease in the density of the samples with increase in Y content can be correlated with the higher level of porosity observed in SEM micrographs.

The lattice parameter variation of Y-free and Y-added samples are shown in figure 3.13. With the increase in Y content, a systematic contraction in c-axis length is observed, while there is no appreciable change in the a/b axes length for $0.1 \leq x \leq 0.5$. This reveals that the structure of pure (Bi,Pb)-2212 superconductor having an orthorhombic symmetry transforms to pseudo
Figure 3.13: Variation of lattice parameters as a function of added Y stoichiometry
tetragonal symmetry for $0.1 \leq x \leq 0.5$. Thus, a slight structural transformation is induced in the Cu-O bond length in the CuO$_2$ plane as a function of Y content. Also, Y doping imparts additional charge carriers which incorporates excess oxygen into Bi-O layer leading to an increase in oxygen content in the (Bi,Pb)-2212 structure. This induces a contraction in Bi-O layers, which can be attributed to the contraction of c-axis length.

Figure 3.14 shows the temperature dependence of normal state resistivity of Y-free and Y added samples for varying Y content from $x = 0$ to 0.5. All the samples show superconductive transitions. For the Y-free sample a pseudo transition occurs at around $\sim 110$ K as indicated by a slight drop in resistance. This may be due to the coexistence of the high $T_c$ phase (Bi,Pb)-2223 in very low percentages which could not be detected in the XRD analysis. Also it is found that as the Y content increases, the normal state resistivity of the samples increases while the residual resistivity ratio (RRR) decreases considerably (Figure 3.15). Figure 3.16 shows the variation of $T_c$ and $J_c$ as a function of Y stoichiometry of superconducting samples up to $x = 0.5$. The $T_c$ increases with
increase in Y doping. The maximum $T_c$ obtained is 97.4 K for Y3 sample and thereafter $T_c$ decreases gradually as the Y content increases. The variation $\Delta T_c$ is given in table 3.4. It shows that $\Delta T_c$ increases initially, reaches a maximum for $x = 0.1$ and thereafter decreases slightly for $0.2 \leq x \leq 0.5$ samples. The large transition width ($\Delta T_c$) observed is due to the change in resistive state of Bi-O layer resulting in the partial isolation of CuO$_2$ layers across the charge reservoir plane (Bi-O layers) [43,44] as a result of Y addition. The temperature coefficient of resistance $\alpha(T)$ at normal state of pure and Y added (Bi,Pb)-2212 samples is shown in table 3.4. The observed decrease in $\alpha(T)$ and RRR values as a function of Y stoichiometry indicates the decrement in the charge carrier density (holes) in (Bi,Pb)-2212 system, which in turn increases the normal state resistivity of the sample as a whole.

The $J_c$ is found to increase significantly with Y doping (Table 3.4). The maximum $J_c$ obtained is 696 A/cm$^2$ at 64 K for Y2 sample, while the Y-free sample shows a $J_c$ of 101 A/cm$^2$ i.e. only $\frac{1}{7}$th of the maximum. It was observed that Y3 measured a maximum $T_c$, but its $J_c$ (562 A/cm$^2$) is slightly less than Y2 and this is attributed to the increased porosity, misorientation and shortening of (Bi,Pb)-2212 grains. However, the significant enhancement in $J_c$ observed in general for the Y added samples cannot be attributed to any improvement in microstructure, since pure (Bi,Pb)-2212 sample (YO) exhibits the best microstructure compared to all the Y added samples.

The enhancement in $T_c$ and $J_c$ of Y added samples are related to the chemical as well as electronic rearrangement introduced due to the dual effect of Y and Pb co-doping in Bi-2212. From the previous section 3.3, it can be seen that there is no appreciable change in $T_c$ of Bi-2212 due to the solo substitution of Pb in Bi-site. The hole carrier density of pure Bi-2212 estimated is 0.37 holes/CuO$_2$ [45] which is overdoped. The effect of Y addition on $T_c$ is attributed to the change in hole concentration. When Y is added in (Bi,Pb)-2212 system, they are expected to occupy the Ca/Sr site due to their comparable
Figure 3.14: Temperature dependent normalized resistivity plots of Y added samples.
ionic size (Ca$^{+2} = 0.93$ Å, Sr$^{+2} = 1.21$ Å and Y$^{+3} = 0.89$ Å). This is evident from the phase assemblage data of the samples particularly at higher doping
concentrations \( x = 0.4 \) and \( x = 0.5 \) and the systematic shrinkage observed in the c-axis parameter with Y addition. The replacement of \( \text{Ca}^{+2}/\text{Sr}^{+2} \) by \( \text{Y}^{+3} \) ion would result in lowering of the hole concentration from the overdoped pure \((\text{Bi,Pb})-2212\) to an optimum value at \( x = 0.3 \) leading to the maximum \( T_c \). As the dopant concentration increases further \( (x > 0.3) \), the hole carrier concentration decreases and the system goes to underdoped region resulting in lowering of \( T_c \). The electrical conductivity of the blocking layers of Bi-2212 can be systematically enhanced by Pb doping into the blocking layers (Bi-O) [9]. Also, the anisotropy can be substantially reduced by the Pb doping [9, 10]. This increases the Josephson coupling strength between the CuO\(_2\) layers across the insulating Bi-O layers [11] thereby increasing c-axis conductivity and as a result the \( J_c \) increases to a maximum. Also, the point defects introduced by the substitution of \( \text{Y}^{+3} \) at \( \text{Ca}^{+2}/\text{Sr}^{+2} \) sites can act as flux pinning centers, which can enhance the self field \( J_e \). For higher Y contents, excess oxygen ions are incorporated into the oxygen deficient Bi-O layers which make it more insulating. This increases the c-axis resistivity, hence weakening the Josephson coupling strength between the CuO\(_2\) layers across the Bi-O layers resulting in reduction of self field \( J_c \) at higher \( x \). Thus it is shown that Y and Pb co-doping

Table 3.4: \( \Delta T_c \), Lotgering index \( (F) \), Self field \( J_c \) (at 64 K) and temperature coefficient of resistance \( (\alpha) \) at normal state of pure and Y added (Bi,Pb)-2212 samples

<table>
<thead>
<tr>
<th>Y Content</th>
<th>( \Delta T_c ) (K)</th>
<th>Lotgering Index ( (F) )</th>
<th>( J_c ) at 64 K (A/cm(^2))</th>
<th>( \alpha(T) ) ((10^{-4}/K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.45</td>
<td>0.76</td>
<td>101</td>
<td>2.70</td>
</tr>
<tr>
<td>0.1</td>
<td>14.6</td>
<td>0.65</td>
<td>497</td>
<td>1.67</td>
</tr>
<tr>
<td>0.2</td>
<td>13.0</td>
<td>0.60</td>
<td>696</td>
<td>1.39</td>
</tr>
<tr>
<td>0.3</td>
<td>10.7</td>
<td>0.58</td>
<td>562</td>
<td>1.42</td>
</tr>
<tr>
<td>0.4</td>
<td>10.6</td>
<td>0.45</td>
<td>484</td>
<td>1.25</td>
</tr>
<tr>
<td>0.5</td>
<td>10.1</td>
<td>0.41</td>
<td>40</td>
<td>0.94</td>
</tr>
</tbody>
</table>
in Bi-2212 enhances the superconducting properties of the system to a great extent.

3.5 Summary and Conclusions

Pb-substitution at the Bi-site enhances the self-field $J_c$ while slightly deteriorates the $T_c$ of the Bi-2212 superconductor. The maximum value of the bulk $J_c$ of the Pb-doped ($x = 0.5$) Bi-2212 sample is $\sim 3$ times higher than undoped sample. The enhancement of $J_c$ is found to be due to the improved microstructure and the increase in the c-axis conductivity of the system. Considering the fact that the best results are obtained for the Pb content in the range $x = 0.4 - 0.5$, this composition is chosen for further work presented in the forthcoming chapters.

The studies on the effects of Y addition in Pb doped Bi-2212 show that $Y^{+3}$ ions enter into the crystal structure replacing $Ca^{+2}$ and $Sr^{+2}$, thereby reducing hole concentration in the electronic structure of the system. Pb co-doping results in the reduction of c-axis resistivity due to the strong Josephson coupling between CuO$_2$ layers at lower Y contents. The $T_c$ and $J_c$ are significantly enhanced for optimum Y concentration. The maximum $T_c$ is obtained for the sample with $x = 0.3$ and $J_c$ for the sample with $x = 0.2$ in the stoichiometry Bi$_{1.7}$Pb$_{0.4}$Sr$_{2.6}$Ca$_{1.1}$Cu$_{2.1}$Y$_x$O$_{8+\delta}$. At higher doping levels secondary phases containing Ca and Sr are observed. The changes in the electrical and superconducting properties are due to the changes in the structural as well as electronic properties induced by Pb and Y co-doping.
References


