EFFECT OF Pb ON STRUCTURAL AND SUPERCONDUCTING PROPERTIES OF RE MODIFIED Bi-2212*

5.1. Introduction

The idea of substituting Pb for Bi in BSCCO is rather natural, since the Pb and Bi cations have similar radii and both can easily occupy octahedral sites. Further more it appeared that a copper valance greater than 2⁺ was necessary for superconductivity. A simple way of increasing the apparent valance of Cu would be to replace some of the Bi³⁺ by Pb²⁺. The effect of Pb substitution on the structure and superconductivity has been reported by several groups. X-ray powder diffraction patterns from Pb substituted Bi-2212 [(Bi,Pb)-2212] samples show same reflections with similar intensities indicating that the basic structure is unchanged by Pb-substitution and Pb-atoms occupies the Bi-sites. Since the scattering power of Bi and Pb are quite similar, it would be very difficult to determine the degree of substitution by XRD. However the maximum solubility limit of Pb in Bi-2212 corresponds to the formula Bi₁₄Pb₀₄Sr₂CaCu₂O₈₊₀ [1] and larger amounts of Pb produce Pb-based impurity phases, which can be detected in XRD. Several investigations have pointed out that Pb substitution affects the structural modulation [2-6]. The characteristic incommensurate modulation associated with BSCCO materials increased by Pb addition [5, 6]. Recent 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, the structural modulation becomes infinite (no modulation). As a result the anisotropy of modulation free crystals is strongly reduced [7]. The out-of-plane resistivity decreases by four orders of magnitude in Pb-doped crystals [8]. Substitution of Pb leads to the replacement of Bi³⁺ by Pb²⁺ ions and this decreases the oxygen content. The introduced divalent Pb²⁺ ions leads to less additional oxygen in Bi-O layer and yields a longer periodicity of

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modulation. Thus the reason for structural modulation is the presence of additional oxygen atoms in the Bi-O layers \(^9, 10\). The replacement of trivalent Bi\(^{3+}\) by divalent Pb\(^{2+}\) increases the hole concentration on the Cu-O\(_2\) planes. This explains the slight decrease in \(T_c\) with Pb substitution. But there are reports \(^11, 12\) on the hole-doping point of view that Pb incorporation does not affect the carrier concentration significantly.

Almost all previous RE doping studies are on Bi-2212 without Pb. Such studies demonstrate that \(T_c\) slightly increases up to an optimum level of RE substitution \(^14-12\). Effects of doping of rare earth (RE) ions, in the crystal and electronic structure, thermal properties and on the superconducting properties such as \(T_c\) in Bi-2212 system are also studied \(^13-23\). In chapters 3 and 4 we have reported that \(T_c\) and self field \(J_c\) of RE added (Bi,Pb)-2212 are highly enhanced. In this chapter we discuss the effect of Pb on structural and superconducting properties of RE-added Bi-2212.

5.2. Experimental

Rare earth added superconductor with a general stoichiometry of Bi\(_{2+x}\)Pb\(_x\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)O\(_{y}\) (where \(x = 0\) and 0.4 and RE = La, Gd and Yb) were prepared by conventional solid state synthesis route using high purity carbonates and oxides of the ingredients. The RE are chosen in such a way that they are from left, middle and right end of the periodic table with different ionic size. The pellets of the samples are prepared as explained in chapter 3 and were then heat treated at 845 °C for 120 h (60+60) h at a heating rate of 4 °C/minute in two stages with one intermediate pressing under a force of 60 kN.

Phase analysis of the samples was done using XRD. Phase identification was performed using 'X’Pert high score' software. Microstructural examinations of the samples were done using SEM and elemental analyses of the samples were done using EDX. The densities of the pellets before and after the two stages of sintering were calculated by measuring the mass and dimensions of the pellets. The \(T_c\) and \(J_c\) of the samples were measured by four probe method.

The samples are identified as Bi\(_{2.1}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)O\(_{y}\) (PBO), Bi\(_{1.7}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)O\(_{y}\) (PB), Bi\(_{2.1}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)La\(_{0.25}\)O\(_{y}\) (PB0La), Bi\(_{1.7}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)La\(_{0.25}\)O\(_{y}\) (PBLa), Bi\(_{2.1}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)Gd\(_{0.25}\)O\(_{y}\) (PB0Gd), Bi\(_{1.7}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)Gd\(_{0.25}\)O\(_{y}\) (PBGd), Bi\(_{2.1}\)Sr\(_2\)Ca\(_{1.1}\)Cu\(_{2.1}\)Yb\(_{0.25}\)O\(_{y}\) (PB0Yb).
5.3. DTA analysis

Fig. 5.1. DTA plots of the samples

Fig. 5.1 shows the DTA plots of the different samples taken in air at a rate of 10 °C/min. Two endothermic peaks with the first one (small) due to the formation and the second (large) due to the melting of Bi-2212 are observed for all the samples. Plots of the samples without RE show sharp second endothermic peaks, which represents the...
sharp melting point of the system. It is clear from the positions of the peaks that doping of Pb decreases both the formation and melting temperatures. But RE addition increases and broadens these temperatures. The broadening is maximum for Gd addition and shifting is maximum for Yb. The reasons for the shifting are explained in chapter 3. In the RE added samples also the Pb doping decreases the formation temperature of Bi-2212. Thus one advantage of Pb in Bi-2212 is that it reduces the formation temperature of the pure and RE doped Bi-2212.

5.4. XRD analysis

![XRD patterns](image)

**Fig. 5.2.** XRD patterns of (a) powder and (b) pellets after final stage heat treatment

Fig. 5.2 (a) shows the XRD patterns of the powdered samples and (b) that of the corresponding pellets after the last stage heat treatment. In these patterns all other phases except Bi-2212 disappeared. This indicates that the doped Pb and RE enter into the Bi-2212 structure. No secondary phase containing RE is observed in the XRD patterns. From the XRD patterns the c-axis length and the cell volume are calculated.
assuming orthorhombic symmetry to Bi-2212. These values are shown in Table 5.1. The c-axis contraction is higher for smaller RE ion, Yb and lesser for larger RE, La. Substitution of Pb at Bi site slightly decreases the c-axis length. From the XRD patterns of the pellets [Fig. 5.2 (b)] it is clear that the grains are highly oriented in the \((00\ell)\) planes. Even though RE addition destroys the grain growth, \((00\ell)\) plane is more oriented in Pb doped samples than Pb free sample. Table 5.1 also shows the Lotgering Index (\(\mathcal{F}\)) and the bulk density. Both \(\mathcal{F}\) and density decreases by RE doping compared to the pure sample. The \(\mathcal{F}\) and density of the Pb doped samples are higher compared to Pb free samples. This indicates the positive effect of Pb in the Bi-2212 in improving the texture and reducing the porosity.

5.5. SEM and EDX analyses

Fig. 5.3 shows the SEM pictures of the fractured surfaces of the pure and RE modified samples with and without Pb taken in the back scattered mode. The grain morphology of the pure sample shows clear and flaky grains with layered growth typical of Bi-2212. Compared to the pure sample the grain size and texturing of the RE doped samples are reduced as seen in previous chapters, but the texturing and layered grain growth of the Pb doped samples are better compared to the Pb free samples. The SEM pictures also support the \(\mathcal{F}\) values. In the EDX spectrum of the RE doped samples the primary phase contains the doped RE. The EDX spectra of the secondary phases are mainly Sr and Ca rich and there is no RE present in the secondary phases. These indicate that the doped RE completely enters into the Bi-2212 structure and substitutes the Sr/Ca site. The EDX spectrum of the relatively large area of the Bi-2212 grains and the secondary phase present in the samples are shown in Figs. 5.4 and 5.5 respectively. Quantitative values of the atomic compositions present in the Bi-2212 grains when Cu content is taken as 2.1 are given in Table 5.2. These values of the final compositions of Bi-2212 grains show that Bi-2212 grains contain the REs with lesser amount of Sr and Ca.
Fig. 5.3. SEM fractographs of the samples taken in back scattered mode
Fig. 5.4. EDX spectra of the Bi-2212 grains of the samples
Table 5.1. Different parameters of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$c$-axis (Å)</th>
<th>Density (g/cm$^3$)</th>
<th>Lotgering index (£)</th>
<th>$T_{C\text{-onset}}$ (K)</th>
<th>$T_{C\text{-super}}$ (K)</th>
<th>$\Delta T_C$ (K)</th>
<th>$\rho_{(300)}$ (µΩm)</th>
<th>$J_C$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0</td>
<td>30.82</td>
<td>5.29</td>
<td>0.84</td>
<td>80.6</td>
<td>77.6</td>
<td>3.0</td>
<td>9.6</td>
<td>108.7</td>
</tr>
<tr>
<td>PB</td>
<td>30.80</td>
<td>5.31</td>
<td>0.87</td>
<td>75.0</td>
<td>69.6</td>
<td>5.4</td>
<td>9.5</td>
<td>95.1</td>
</tr>
<tr>
<td>PB0La</td>
<td>30.78</td>
<td>4.95</td>
<td>0.74</td>
<td>95.1</td>
<td>81</td>
<td>14.1</td>
<td>23.0</td>
<td>223.5</td>
</tr>
<tr>
<td>PBLa</td>
<td>30.79</td>
<td>5.98</td>
<td>0.78</td>
<td>91.5</td>
<td>85</td>
<td>6.5</td>
<td>22.5</td>
<td>676.0</td>
</tr>
<tr>
<td>PB0Gd</td>
<td>30.75</td>
<td>5.00</td>
<td>0.65</td>
<td>95.3</td>
<td>81</td>
<td>14.3</td>
<td>31.9</td>
<td>175.8</td>
</tr>
<tr>
<td>PBGd</td>
<td>30.72</td>
<td>5.18</td>
<td>0.76</td>
<td>92.2</td>
<td>85</td>
<td>7.2</td>
<td>20.5</td>
<td>580.0</td>
</tr>
<tr>
<td>PB0Yb</td>
<td>30.70</td>
<td>4.84</td>
<td>0.61</td>
<td>97.6</td>
<td>83.1</td>
<td>14.5</td>
<td>47.1</td>
<td>169.0</td>
</tr>
<tr>
<td>PBYb</td>
<td>30.68</td>
<td>5.18</td>
<td>0.71</td>
<td>93.6</td>
<td>86.3</td>
<td>7.3</td>
<td>25.1</td>
<td>688.0</td>
</tr>
</tbody>
</table>
Fig. 5.5. EDX spectra of the secondary phases present in the samples

Table 5.2. Elemental compositions of the samples when Cu content is taken as 2.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi</th>
<th>Pb</th>
<th>Sr</th>
<th>Ca</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0</td>
<td>2.1</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>PB</td>
<td>1.63</td>
<td>0.34</td>
<td>1.99</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>PB0Gd</td>
<td>1.9</td>
<td>0</td>
<td>1.7</td>
<td>0.88</td>
<td>0.27</td>
</tr>
<tr>
<td>PBGd</td>
<td>1.5</td>
<td>0.30</td>
<td>1.6</td>
<td>0.80</td>
<td>0.25</td>
</tr>
<tr>
<td>PB0La</td>
<td>2.2</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.27</td>
</tr>
<tr>
<td>PBLa</td>
<td>1.6</td>
<td>0.32</td>
<td>1.72</td>
<td>0.8</td>
<td>0.22</td>
</tr>
<tr>
<td>PB0Yb</td>
<td>2.1</td>
<td>0</td>
<td>1.95</td>
<td>1.0</td>
<td>0.29</td>
</tr>
<tr>
<td>PBYb</td>
<td>1.62</td>
<td>0.33</td>
<td>1.7</td>
<td>0.85</td>
<td>0.26</td>
</tr>
</tbody>
</table>
5.6. Superconducting properties

Fig. 5.6. R-T plots of the different samples

The R-T plots of the different pure and RE added samples with and without Pb are shown in Fig. 5.6. The room temperature resistivity at 300 K ($\rho_{300}$) of the samples are found out from the R-T plots are listed in Table 5.1. It is clearly seen that all the Pb doped samples show less resistivity than samples without Pb. A partial transition occurs near 110 K only for the Pb doped sample without RE due to the existence of high $T_c$ Bi-2223 phase in very small percentages. Fig. 5.7 shows the R-T plots of the samples in the transition region to get a clear view of the transition width. The $T_{c\text{cont}}$
of the samples PB0 and PB doesn’t have much change, but the $T_{C\text{-zero}}$ of PB0 has a higher value comparing with that of sample PB and hence the $\Delta T_c$ increases from 3 K to 5.4 K when Pb is doped in the pure sample. All the RE doped sample show higher $T_{C\text{-zero}}$ and $T_{C\text{-onset}}$ comparing with samples PB0 and PB. But Pb addition decreases $T_{C\text{-onset}}$ and increases $T_{C\text{-zero}}$ in RE doped samples comparing with RE free samples and hence Pb addition in RE doped samples decreases the transition width considerably. The values of $T_{C\text{-zero}}$, $T_{C\text{-onset}}$ and $\Delta T_c$ found from the $R$-$T$ plots are shown in Table 5.1. These results show that combined effect of Pb and RE in Bi-2212 increases $T_c$ considerably along with significant reduction in $\Delta T_c$. This shows that the co-doping reduces inhomogenety in the crystal grains comparing with the doping of Pb alone or RE alone, because inhomogenety in material leads to broadening of the transition from the superconducting to the normal state.

![Graphs showing $R$-$T$ plots](image)

**Fig. 5.7.** $R$-$T$ plots of the different samples near the transition region
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In RE doped samples some of the doped RE$^{3+}$ ions replace the Ca$^{2+}$ or Sr$^{2+}$ ions and as a result the hole carrier concentration decreases to an optimum level and hence the $T_{C\text{-onset}}$ increases. In the case of most of the RE doping the optimum doping level is $x = 0.2-0.3$. The doping of Pb$^{2+}$ ions for Bi$^{3+}$ slightly increases the hole carrier concentration and hence the $T_{C\text{-onset}}$ decreases. The reduced $\Delta T_c$ value and the reduced room temperature resistivity of the Pb doped samples are due to the reduced electromagnetic anisotropy and increased conductivity by Pb doping. The self-field $J_c$ of RE doped samples slightly enhances but for the co-doped samples with Pb and RE, the $J_c$ is highly enhanced. Table 5.1 shows the self field $J_c$ values of the samples at 64 K. The result shows that the self field $J_c$ due to RE doping slightly enhances but co-doping of Pb and RE highly improves superconducting properties of Bi-2212 system. Even though RE addition alone shifts the system from 'over-doped' state to 'optimally-doped' state and thus increases $T_c$, its inhomogenity also increases. Pb addition alone reduces anisotropy and improves conductivity but doesn’t change $T_c$. But co-doping of Pb and RE increases $T_c$, reduces inhomogenity and enhances $J_c$. In chapter 6 we will see that the co-doping gives sufficient pinning of the vortices, which also helps to enhance $J_c$.

5.7. Conclusion

The structural and transport properties of Pb free and Pb doped RE added Bi-2212 were studied. The $\xi$ value of the samples decreases with RE addition but increases with Pb addition. The c-axis length and cell volume changes slightly with Pb doping in pure and RE added samples. Density of Pb doped samples is higher comparing with Pb free samples. $T_{C\text{-onset}}$ and $T_{C\text{-zero}}$ highly enhances with RE addition in Pb free and Pb added samples. Pb free samples show higher $T_{C\text{-onset}}$ comparing with Pb doped samples but Pb doped samples shows higher $T_{C\text{-zero}}$ comparing with Pb free samples. Thus co-doping of Pb and RE in Bi-2212 critically adjust the transition width to a low value compared to the RE alone doped system. RE addition enhances self field $J_c$ but highly enhance co-doping of Pb and RE. The combined effect of Pb and RE improves inhomogenity, reduces anisotropy and porosity, improves conductivity and flux pinning than samples added with RE alone.
References


