CHAPTER V

EFFECT OF SILVER ADDITION TO BPSCCO SYSTEM
5.1 INTRODUCTION

High temperature superconductors have high potential in the area of high magnetic field applications. For using these materials in magnets the material has to be fabricated in the form of wires or tapes. These wires should be capable of carrying high currents in presence of high magnetic fields i.e., wires should have high critical current \( (J_c) \) and upper critical field \( (H_{c2}) \). High-\( T_c \) materials are ceramics and very brittle, hence cannot be drawn in the form of wires/tapes as such. For drawing wires of such materials some cladding material is required which should not react with the core material and should be a good conductor. Copper (Cu) has been used for the purpose in case of conventional superconductors, but being a component in all high-\( T_c \) materials copper cannot be used as a cladding material. Silver is proven to be a very good cladding material for rare-earth based superconductors and is being used as a cladding material for drawing wires. It is reported that silver does not react with 123 material up to 60 wt% addition [1].

Though silver is being used even for Bi-based superconductors [2] but the exact reaction of silver with Bi based superconductors B(P)SCCO is not clearly understood. Contradictory results have been reported by different groups. For example, Jin et al [3] find silver nonpoisonous up to a
concentration of 20 wt% in a Bi$_{4}$Sr$_{3}$Ca$_{2}$Cu$_{4}$O$_{16+x}$ compound. A decrease in $T_c$ from 74.8K to 63.7K is reported by Lin and Chen [4] when 50 vol.% silver is added to a 2212 composition of the BSCCO system. At 60 vol.% silver superconductivity disappears completely. Dou et al [5] find a strong depression of $T_c$ of the 2223 (110K) phase of the BPSCCO system with the addition of silver when the specimen is sintered in oxygen or air. $T_c$, however, remains unaffected if the specimen is sintered under low oxygen pressure (< 0.67 atm.). No degradation in the $T_{c0}$ (zero resistivity) of the BPSCCO system is reported by Mukherjee et al [6] up to a silver addition of 37 wt% when sintered in air. Svoboda et al [7] report that silver up to 20 wt% in BPSCCO system does not influence the superconducting properties as such but affects rather strongly the intergrain coupling behaviour. Above 10 wt% silver the intergrain coupling improves if the sintering is carried out for prolonged period (264 hours at 840°C). We thus find that divergent results have been reported on the effect of silver addition to the B(P)SCCO system. This calls for further studies on this topic.

5.2. EXPERIMENTAL: The compound Bi$_{1.6}$Pb$_{0.4}$Sr$_{1.6}$Ca$_{2}$Cu$_{3}$Y$_{y}$ was prepared by solid state ceramic technique. Various amounts of AgNO$_3$ corresponding to a silver ratio of 5,10,20 and 50% by weight is added to the master compound, details are given in Chap.II (sec. 2.1.f). All the specimens were sintered at 810°C
for 24 hours and furnace cooled to room temperature.

Resistance and thermoelectric power (TEP) are measured in the same way as described in Chap.2, in the temperature range of 78K to 300K. Room temperature XRD patterns are recorded in 2θ range of 3° to 45° using CuKα radiation in order to study the effect of silver on the phase formation. SEM photographs are taken on the fractured surface of the specimen to see the effect on grain morphology.

5.3.RESULTS AND DISCUSSION: The resistive transition of all the specimens is shown in Fig.(5.1). The BPSCCO specimen A without

Fig.5.1. Normalized resistance vs. temperature plots for Ag added specimens.
silver addition has the onset $T_c$ of 110K and $T_{c0}$ (zero resistance) at 102K. All other specimens (B to E) with increasing silver addition though have the same onset temperature of 110K, nevertheless have a resistance tail at the lower temperature end of the curves. The $T_{c0}$ of the specimens decreases with increasing silver concentration. For clarity the $T_c$(onset), $T_c$(midpoint) and $T_{c0}$(zero resistance) are plotted in Fig. (5.2) against silver concentration. It is seen from the Fig.(5.1)

Fig. 5.2. $T_c$(onset), $T_c$(mid point), $T_{c0}$(zero resistance temperature) plotted against Ag concentration.
that the onset $T_c$ remains unchanged at 110K with silver addition. This indicates that even for large silver addition (up to 50 wt%) the 2223 phase structure remains unchanged. The $T_c$(mid) and $T_{c0}$, however, show systematic drop in values as also seen in Table 5.1. The drop in $T_{c0}$ value is rather large as silver concentration is increased.

**TABLE 5.1**

Values of $T_c$ (onset), $T_c$(mid), $T_{c0}$ and relative volume fraction of 2223 phase are tabulated for different concentrations of Ag. Relative volume fraction of high-$T_c$ phase (HTF) is calculated from (105) reflections of 2212 and 2223 phases.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Ag Concentration(wt%)</th>
<th>$T_c$(onset)</th>
<th>$T_c$(mid)</th>
<th>$T_{c0}$</th>
<th>HTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>110</td>
<td>105</td>
<td>102</td>
<td>64</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>110</td>
<td>103</td>
<td>93</td>
<td>69</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>110</td>
<td>103</td>
<td>88</td>
<td>63</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>110</td>
<td>102</td>
<td>81</td>
<td>72</td>
</tr>
<tr>
<td>E</td>
<td>50</td>
<td>110</td>
<td>100</td>
<td>76</td>
<td>36</td>
</tr>
</tbody>
</table>

Fig.(5.3) gives the XRD plots of all the specimens. Most of the diffraction peaks can be indexed to the two superconducting phases viz., the high $T_c$ 2223 phase and the low $T_c$ 2212 phase. In addition to these two phases peaks corresponding to the Ca$_2$PbO$_4$ and CuO are also observed in all the specimens. The relative fraction of the 2223 phase is estimated from the intensities of the (105) reflections. This was done to avoid the problem of preferred orientations invariably associated with the (001) reflections. As seen from the Table 5.1 the high
Fig. 5.3. Room temperature XRD patterns for Ag added specimens in 2θ range of 3° to 45°. Intensity of reflections corresponding to Ag gradually increases with increasing Ag concentration.
$T_c$ 2223 phase fraction varies between 64 and 72% for specimens with 0 and 20 wt% silver respectively. For specimen E, having 50 wt% silver, the 2223 phase fraction drops to 32%. The intensities of the $\text{Ca}_2\text{PbO}_4$ and CuO peaks are also reduced drastically for the specimen (E). It is reported in the literature [8] that in a calcium rich BPSCCO-system the presence of the $\text{Ca}_2\text{PbO}_4$ and CuO reactive liquid phases leads to the formation of the 2223 phase as a result of the reaction of the liquid phase with the 2212 phase. The 2223 phase is believed to be distributed along grain boundaries of the 2212 phase and forms a conducting network. Silver probably diffuses along the grain boundaries of the 2223 phase weakening the intergrain coupling as confirmed by the appearance of a tail at the lower temperature end of the transition curve. As the silver concentration is increased it diffuses further to wet the 2212 grains and prevent the reaction between the 2212 phase and the liquid phase. This will reduce the 2223 phase fraction as is observed in the present measurement for the specimen E (Table 5.1). The results of XRD are very similar to results for rare earth based system, where silver seems not to affect the phase formation as well as transition temperature.

TEP for all the specimens is positive and either changes sign or has a tendency to change the sign from positive to negative at higher temperatures and has been plotted against temperature in Fig.5.4. TEP for all the specimens shows a
maxima at $T_m$ which is about 125-130K, except for the specimen with highest dopant level where maxima occurs at about 115K.

**Fig. 5.4. TEP vs. temperature plots for Ag added specimens.**

Above this maxima TEP is a decreasing function of temperature and below maxima it goes down to zero at $T_{m0}$ which is about 110K.

**TABLE 5.2**

Maximum value of TEP ($S_m$), TEP peak temperature ($T_m$), zero TEP temperature ($T_{m0}$) and zero resistance temperature ($T_{c0}$) are tabulated for different concentrations of Ag.

<table>
<thead>
<tr>
<th>Ag Concentration (wt%)</th>
<th>$S_m$ ($\mu$V/K)</th>
<th>$T_m$ (K)</th>
<th>$T_{m0}$ (K)</th>
<th>$T_{c0}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.0</td>
<td>125</td>
<td>103</td>
<td>102</td>
</tr>
<tr>
<td>5</td>
<td>9.6</td>
<td>125</td>
<td>103</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>8.0</td>
<td>120</td>
<td>103</td>
<td>88</td>
</tr>
<tr>
<td>20</td>
<td>5.8</td>
<td>120</td>
<td>103</td>
<td>81</td>
</tr>
<tr>
<td>50</td>
<td>4.6</td>
<td>115</td>
<td>103</td>
<td>78</td>
</tr>
</tbody>
</table>
103K for all the specimens. Maximum value of TEP $S_m$ decreases with increasing silver concentration. The maximum values for all the specimens are 11, 9.6, 8, 5.8 and 4.6 $\mu$V/K for silver concentration of 0, 5, 10, 20 and 50 wt% respectively. In Table 5.2 values of $T_c$, $T_m$, $S_m$ and $T_{s0}$ are summarized.

The fact that the onset $T_c$ remains unaffected with the silver addition of as much as 50 wt% indicates the nonreactive nature of silver in the BPSCCO system. The substitution of silver on any site in the BPSCCO system can, indeed be ruled out on the basis of the following considerations. Silver is not likely to substitute for the Bi-site or the Cu-site firstly because $\text{Ag}^{2+}$ or $\text{Ag}^{3+}$ is a highly oxidizing species and no ternary oxides of silver (Bi-Ag-O or Cu-Ag-O) are known in which silver has a valency of $\pm 2$. Binary oxide $\text{AgO}$ is, however, known but this can be prepared only under high pressure and high temperature conditions. Secondly $\text{Ag}^{1+}$ is a 4$d^{10}$-system and always prefers a 2-fold linear coordination but never a square planer, pyramidal or octahedral coordination which are the normally available sites in the BPSCCO system. Similarly no ternary oxides such as $\text{Sr-Ag-O}$ or $\text{Ca-Ag-O}$ are known to exist. The only possibility that exists, is the formation of ternary oxides $\text{Ag}_2\text{PbO}_2$ and $\text{Ag}_5\text{Pb}_2\text{O}_6$ [9,10] which can form as second phases in an oxidizing atmosphere by leaching out part of lead from the BPSCCO (2223) system leaving vacancies in the $\text{Bi}_2\text{O}_2$ layers. This also does not seem to occur in the present case because Bi-ion vacancies will affect the Cu-valency and hence
the hole concentration and the $T_c$. This is contrary to the present data which do not show any change in the onset $T_c$ of any specimen. This conclusion is also supported by the absence of diffraction peaks of these compounds ($\text{Ag}_2\text{PbO}_2$ and $\text{Ag}_5\text{Pb}_2\text{O}_6$) in the XRD spectra of these specimens (Fig. 5.3). The presence of a very small quantity of these compounds, (within the X-ray diffraction limit) however, may not be totally ruled out as the silver can react with $\text{Ca}_2\text{PbO}_4$ to form this compound. This can then be a possible reason for the reduced intensity of the $\text{Ca}_2\text{PbO}_4$ compound in specimen E having 50 wt% silver. The presence of small concentration of such insulating phases can also account for the observed decrease in the slope of the resistance-temperature curves (Fig. 5.1).

The appearance of a tail in the low temperature end of the resistive curves and the consecutive decrease of $T_{c0}$ is thus probably caused by the diffusion of silver along the grain boundaries, discussed earlier, weakening the superconducting intergrain links. At high concentration silver wets and increasingly envelopes the superconducting grains making the intergrain links resistive. The SEM pictures in Fig. (5.5) clearly show that 50 wt% silver wets and envelopes large number of grains. As the temperature is reduced the Josephson coupling energy increases in comparison to the thermal energy ($k_B T$) until at a temperature $T_{c0}$ the conducting path (via Josephson coupling between the grains) is established and the resistance
Fig. 5.5. SEM micrographs for Ag added specimens with Ag addition of 0, 10 and 50 wt%.
drops to zero. As silver concentration is increased the tail becomes longer and $T_c$ shifts to lower temperature. The question then arises as to why a similar effect is not observed in the YBCO system, for a similar range of silver addition (0-60 wt%), $T_c$ of the YBCO-system remains unchanged [1] and no tail appears in the resistive transition. The possible answer lies in the fact that the 2223 phase of the pure BPSCCO system has a low density ($\approx 3.5$g/cc) after the first sintering and thus has a large porosity. It is only after the repeated pressing and sintering that an improved density close to theoretical value is achieved. Silver thus diffuses through the grain boundaries and large pores. This weakens the intergrain coupling which results in the observed resistive transition behaviour. Since the problem of low density is not faced in the 2212 phase of the BSCCO system, the tail effect in the resistive transition has thus not been observed in a 2212 BSCCO-system by Jin et al [3].

TEP of all the specimens can be explained well by using the formula obtained by MFL hypothesis in the same way as has been explained for Sb and Li doped specimens in Chap.IV. According to MFL, TEP is given as

$$S_d = \frac{\pi^2}{2} \left( \frac{k_B}{e} \right) \left( \frac{k_B T}{c_f} \right) \left[ 1 + \ln \frac{k_B T}{\hbar \omega_c} \right]^2$$
where $\lambda$ is dimensionless coupling constant, $\epsilon_f$ is the Fermi energy of the system and $\hbar \omega_c$ is cutoff frequency.

If we plot $(S/T)^{1/2}$ vs. $\ln T$ for the specimens B and C, these plots are nice straight lines as shown in Fig. 5.6. The values of 50 wt% silver added specimen which show negative values at higher temperatures (above 180K) cannot be explained.
well by this formula. The change of sign of TEP is not very obvious using this kind of formalism. The values of parameters $\lambda$, $\hbar \omega_c$, $\varepsilon_f$ are given in Table 5.3. If phonon-drag term is taken into consideration the formula for TEP can be written as

$$S = S_d + \frac{B}{T}$$

then the value of $\varepsilon_f$ changes as given in Table 5.3 along with other parameters. The parameters vary systematically with silver concentration quite similar to the Li and Sb doped specimens. Fig.5.7 shows the experimental values of TEP for pure and 10 wt% Ag added specimens along with theoretical values plotted against temperature. Theoretical values are in good agreement with the experimental values.

**TABLE 5.3**

Values of coupling constant ($\lambda$), estimated value of Fermi energy ($\varepsilon_f$), cutoff frequency ($\hbar \omega_c$) and phonon drag coefficient $B$ are tabulated for different concentrations of Ag. Two values of $\varepsilon_f$ correspond to $B=0$ and $B\neq 0$.

<table>
<thead>
<tr>
<th>Ag Concentration (wt%)</th>
<th>$\lambda$</th>
<th>$\varepsilon_f$(K)($B=0$)</th>
<th>$\hbar \omega_c$(K)</th>
<th>$B$((\mu V))</th>
<th>$\varepsilon_f$(K)($B\neq 0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>100000</td>
<td>300</td>
<td>-150</td>
<td>90000</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>100000</td>
<td>300</td>
<td>-150</td>
<td>90000</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>140000</td>
<td>300</td>
<td>-100</td>
<td>130000</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>200000</td>
<td>300</td>
<td>-80</td>
<td>180000</td>
</tr>
</tbody>
</table>

The last and interesting point to be discussed here is, that by
addition of Ag-$T_{c0}$ decreases sharply, whereas $T_{s0}$ is almost same for all the specimens. Even for the 50 wt% silver added specimen where resistance goes to zero at 76K, TEP goes to zero at 103K. This large difference in $T_{c0}$ and $T_{s0}$ can be explained in terms of lower percolation threshold for TEP (to be discussed in detail in Chap.VI).

![Graph showing TEP values](image)

**Fig.5.7.** Theoretical values of TEP obtained from the values of parameters tabulated in Table 5.3, along with measured values of TEP for pure and 10wt% Ag added specimens.

5.4. **CONCLUSIONS:** From these studies following conclusions can be drawn:

(i) Silver addition to Pb doped Bi system decreases $T_{c0}$.
drastically even when a very small amount of Ag is added.

(ii) Ag does not seem to enter the crystal structure.

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

(iv) Value of Fermi energy $\varepsilon_f$ increases with increasing Ag concentration.
REFERENCES


