All life is transformation, It is the adaption of the old to the new challenges.

..... S.Radhakrishnan
INTRODUCTION

After the invention of superconductivity in the Ba-La-Cu-O system by Bednorz and Muller [1], intensive studies have been reported on a variety of oxide ceramics with the general formula \((A_{1-x}B_x)M_bX_c\) where \(A\) is La, Y etc., \(B\) is Ba, Sr etc., \(M\) is Cu and \(X\) is O [2,3]. Later these systems were followed by the reports of even higher \(T_c\) in the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O systems with maximum \(T_c\) reaching above 120 K [4,5]. In the Bi-Sr-Ca-Cu-O system, three superconducting phases [6-13] have been identified as \((2201)\)-phase \((T_c \sim 10\) K), \((2212)\)-phase \((T_c \sim 85\) K), and \((2223)\)-phase \((T_c \sim 110\) K). These three homologous series are represented by the general formula \(Bi_{2}Sr_{2}Ca_{2-x}Cu_{x}O_{2n+4}\) with \(n = 1, 2\) and \(3\) respectively. It was
reported [14,15] that zero resistance temperature above 100 K had the \( n = 3 \) material as the major phase.

Since the discovery of Bi-Sr-Ca-Cu-O system, many difficulties have been experienced in trying to produce a monophase 2223 compound which shows the highest \( T_c \) of 110 K. It has been reported [16] that the volume fraction of high \( T_c \) phase is very sensitive to heat treatment and strongly depends upon the variation of the starting material composition and therefore it is extremely difficult to synthesise the 105-115 K \( T_c \) single phase superconductor from the nominal composition of \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d} \) (2223). Hence several procedures have been employed to increase the volume fraction of the (2223) phase thereby enhancing the \( T_c \) (0) of Bi-Sr-Ca-Cu-O system. They are:

(i) Annealing at very precise temperatures [10],

(ii) Choice of some particular starting compositions [15,17],

(iii) Long time sintering periods [18], and

(iv) Cationic substitution [19].

Among all the methods adopted so far, the last one was found to be the most efficient one. There are several questions about the structural effects of cationic substitutions etc. that are still unanswered. However, the substitution of Pb proves to be beneficial in the achievement of zero resistance above 100 K [20-24]. Pb substitution for Bi was reported to accelerate the formation of 2223-phase and also to enhance the \( T_c \) of Bi-Sr-Ca-Cu-O system [7,25,26]. This was followed by a large number of reports [19,25,27-38] of obtaining \( T_c \sim 110 \) K in the Bi(Pb)-Sr-Ca-Cu-O compounds with varying compositions and heat treatment conditions to raise the volume fraction of high \( T_c \) phase. In all these studies the samples usually contained the impurity phases like 2212, 2201, \( \text{Ca}_2\text{PbO}_4 \) and \( \text{Ca}_2\text{CuO}_3 \) or unreacted oxides besides the 2223 phase. Whether Pb is incorporated into the \( \text{Bi}_2\text{O}_2 \) layer or simply acts as a flux is not clear. However, the results of the band structure calculations suggest that Pb substitution may have some positive influence on the superconducting properties of the Bi-Sr-Ca-Cu-O system [39]. It was also observed that when the sintering temperature increased above 1148 K, the superconducting properties suddenly deteriorated. For the specimens treated at 1153 K, only a weak diamagnetic signal could be detected at 80 K [40].
Even though the substitution of Pb for Bi enhances the formation of Bi-2223 phase and stabilizes it, to obtain a single phase Bi(Pb)-2223 compound, optimum concentration of Pb is essential. In the case of low concentration of Pb, the formation of 2223 phase is not complete whereas higher Pb content leads to the formation of impurity phases like Ca$_2$PbO$_4$. In view of the role of Pb substitution in stabilizing the 2223 phase and structural characteristics of Pb substituted 2223 compound, in the present investigation, a series of samples with different concentrations of Pb, Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ ($0 < x < 0.5$), were prepared by solid state reaction method and their superconductivity behaviour and structural properties were studied.

EXPERIMENTAL

A series of samples with starting composition of Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ ($x = 0, 0.1, 0.2, 0.25, 0.375$ and $0.45$) were prepared by the solid state reaction method under normal atmosphere using 4N pure Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$ and CuO mixed in the desired ratio using an agate mortar and pestle. Fine homogeneous powders are required to obtain dense uniformly sintered bodies, as the densely sintered body probably has good properties as a superconductor [41,42].

The samples were prepared with different Pb concentrations under different heat treatment conditions. The mixed powders were thoroughly ground and heated at $1128 \text{ K}$ in silica crucible for 100 h with intermittent grinding for every 25 h of heat treatment and finally quenched in air. The air quenched samples were ground to a particle size of 100 $\mu$m and pressed to form pellets of 12 mm diameter and 1.5 mm thick under a pressure of 75 kN. At least two pellets of each composition were made. The pellets were sintered in normal atmosphere at $1118 \pm 10 \text{ K}$ for 72 h. The samples were either air quenched or slowly furnace cooled. The samples were black in colour and stable towards exposure to atmosphere.

X-ray diffraction patterns were recorded using Philips X-ray diffractometer with CuK$_\alpha$ radiation. Resistivity measurements were performed on the sintered samples using the standard four-probe technique in the temperature range 303-70 K. The temperature dependence (303-60 K) of ac susceptibility was studied at 317 Hz and at an ac field of 0.05 Oe.
RESULTS AND DISCUSSION

In the compounds with the general formula \( \text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y} \) (0 < \( x < 0.5 \)) the presence of lead (Pb) results in the stabilization of the high \( T_c \) (2223) phase [20]. The high \( T_c \) (110 K) phase is reported to be most stable for Pb substitutions \( x = 0.2 - 0.3 \). For higher \( x \) values impurity phases are formed [43,44]. It was also reported that as sintering times increased, increasing Pb loss was observed and the 2223 phase was converted into 2212 and 2201 low-\( T_c \) phases [45-47].

In the present investigation the samples with higher concentrations of Pb were found to exhibit low \( T_c(0) \) values and the sample with \( x = 0.25 \) showed a highest \( T_c \) of 105 K. The variation of \( T_c(0) \) with the concentration of Pb is shown in Table 10.1. As seen from the table, it was observed that the samples with \( 0.2 < x < 0.3 \) were found to have \( T_c(0) \) values > 100 K. The \( \text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y} \) samples were subjected to different sintering temperatures and periods and the results are summarized in Table 10.2. It is seen from the table that sintering temperature of 1118 K and time of 72 h are essential to obtain \( T_c(0) \) of 105 K.

The X-ray diffraction pattern of the sample with \( x = 0.25 \), sintered at 1118 K for 72 h is shown in Fig.10.1. The majority of the observed reflections were characteristic of orthorhombic structure with lattice parameters: \( a = 0.3866 \) nm, \( b = 0.3753 \) nm and \( c = 3.6566 \) nm which were consistent with those previously reported [48]. The other concentrations of Pb had the same orthorhombic structure with the same lattice parameters. From the XRD pattern it is seen that the majority of the sample contains the high \( T_c \) (2223)-phase with minor percentage of (2212)- and (2201)-phases.

Voltage and current leads were attached to the pellets using silver epoxy. The temperature dependence of electrical resistance for a typical sample (\( x = 0.25 \)) is shown in Fig.10.2. The behaviour is metallic between 303 and 110 K and the electrical resistance starts dropping at about 115 K and becomes zero at 105 K.

Temperature dependence of ac susceptibility of the sample (\( x = 0.25 \)) is shown in Fig.10.3. From the figure it is seen that at room temperature the specimen is Pauli-paramagnetic and on cooling changes to diamagnetic state at 115 K. The
TABLE 10.1: Variation of the transition temperature with the concentration of Pb in Bi$_2$Pb$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ compound sintered at 1118 ± 10 K for 72 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zero Resistivity temp, Tc (0) (±1)K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>85</td>
</tr>
<tr>
<td>Bi$<em>{1.6}$Pb$</em>{0.4}$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>98</td>
</tr>
<tr>
<td>Bi$<em>{1.8}$Pb$</em>{0.2}$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>103</td>
</tr>
<tr>
<td>Bi$<em>{1.75}$Pb$</em>{0.25}$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>105</td>
</tr>
<tr>
<td>Bi$<em>{1.525}$Pb$</em>{0.375}$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>100</td>
</tr>
<tr>
<td>Bi$<em>{1.55}$Pb$</em>{0.45}$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$</td>
<td>90</td>
</tr>
</tbody>
</table>
**TABLE 10.2:** Effect of sintering temperature and time on $T_c$-zero of $\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ ceramic

<table>
<thead>
<tr>
<th>Sintering temperature (K)</th>
<th>Sintering period (h)</th>
<th>$T_c$-Ze</th>
</tr>
</thead>
<tbody>
<tr>
<td>1098</td>
<td>24</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>82</td>
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<tr>
<td></td>
<td>72</td>
<td>100</td>
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<tr>
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<td>96</td>
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<tr>
<td>1118</td>
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<td>70</td>
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<td></td>
<td>48</td>
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<td>72</td>
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<td>1138</td>
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<td>72</td>
<td>94</td>
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<tr>
<td></td>
<td>96</td>
<td>90</td>
</tr>
</tbody>
</table>
Fig. 10.1. X-ray diffraction pattern of $\text{Bi}_1.75\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10 + \delta}$. 
Fig. 10.2. Temperature dependence of electrical resistivity for Bi$_{1.75}$Pb$_{0.25}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$+$\delta$. 
Fig. 10.3. Temperature dependence of ac susceptibility for $\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. 
diamagnetic signal saturated at 105 K. The other concentrations of Pb had the zero resistivity temperature of 85-103 K.

CONCLUSIONS

Lead substitution in Bi-based compounds favours the formation of high $T_c$ materials and hence its doping concentration is optimized. $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ ($0 < x < 0.5$) high $T_c$ compounds were prepared and characterized by studying their structure, temperature dependence of resistivity and ac magnetic susceptibility. Among the samples studied with different Pb concentrations under different heat treatment conditions, the sample with $x = 0.25$, showed a transition temperature of 105 K. The sintering temperature and time for the sample with $x=0.25$ were also optimized. The other samples had the zero resistivity temperature of 85 - 103 K. All the samples had the orthorhombic structure with lattice parameters $a = 0.3866$ nm, $b = 0.3753$ nm and $c = 3.6566$ nm. XRD pattern revealed that the majority of the sample contained the high $T_c$ (2223)- phase with minor percentage of (2212)- and (2201)- phases.
REFERENCES


