Influence of synthesis conditions on the superconducting properties, microstructure and stability of Pb doped Bi-Sr-Ca-Cu-O superconductors

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Abstract : The importance of optimum calcination and sintering conditions in the process of formation of Pb doped Bi-Sr-Ca-Cu-O group of superconductors is demonstrated with special emphasis on the superconducting transition temperature, critical current density and stability of the high-$T_c$ phase. The observed variation of the superconducting properties have been correlated with their microstructure using X-ray diffraction, energy dispersive X-ray analysis and scanning electron microscopy. Also studied is the variation of the superconducting properties as a function of Pb content in these materials. Finally, the samples were tested for the stability of their superconducting properties under simulated conditions of long hours of exposure to moist atmosphere.

The highest zero resistance of $111$ K was recorded for the Bi$_{2}$Sr$_{2}$Ca$_{n}$Cu$_{2}$O$_{2n+4+8}$ compound for $n=3$ and $x=0.5$, when it was sintered at 850°C for 90 hours, after being calcined for two spells of 20 hours and 4 hours at 810°C with grinding and mixing after each interruption. This sample also demonstrated the highest $J_c$ of ~300 A/cm$^2$.

Keywords : Superconductivity, BSCCO 2223 system, degradation.

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1. Introduction

It has been well established [1] that bismuth based superconductors contain a number of distinct phases which can be described by general formula Bi$_2$Sr$_2$Ca$_n$Cu$_{2n}$O$_{2n+4+8}$ with $n=1, 2, 3$. The maximum zero resistance transition temperature ($T_c$) obtainable in the three cases are 20 K for the 2201 phase ($n=1$), 85 K for the 2212 phase ($n=2$) and 110 K for the 2223 ($n=3$) [2].
The effect of Pb doping up to a certain extent in place of Bi is to promote the formation of the high $T_c$ 2223 phase and stabilize the same [3]. But it is very difficult to prepare 2223 phase singly and so it is necessary to optimise the preparation conditions. The next important point is the stability of this phase. Bismuth based superconductors are known to be more stable than yttrium based compound. But the cause of deterioration of the superconducting properties, specially in humid atmosphere, is still not clearly known and well studied.

Several contemporary studies [4-7] have been reported on the effect of Pb substitution on the formation of high $T_c$ phase ($n = 3$) which do not all agree with one another. Among these, Kambe et al [4] have concluded that Pb substitution in the $n = 2$ phase leads to the decrease of $T_c$ whereas for $n = 3$ phase $T_c$ does not change. Subsequently, from X-ray analysis only, it was reported by Horyn and Sikora [5] that for non-substituted material sintering temperature becomes important i.e., on annealing above 865°C, only the low $T_c$ phase i.e., (2212) leads to (2223) type. On the other hand, a comprehensive study of Pb-doping by Yoon and Lee [6] reveals that Pb substitution up to $x = 0.3$ in (Bi$_{1-x}$Pb$_x$)$_2$ increases the formation of high $T_c$ phase, the highest transition temperature obtained by them being 104°C. Although their study includes magnetic susceptibility measurement there were no measurements of $J_c$ the critical current density or degradation on exposition to humid atmosphere. There is another study by Sinha et al [7] who have identified the wet route process with the solutions of constituent nitrates as the best one having $T_c$ value around 108 K.

From the above discussion, it appears that a comprehensive study of $T_c$, $J_c$ and degradation of these oxide ceramics for different amounts of lead substitution, is yet to be performed.

Under these circumstances, in this paper, we have undertaken a detailed study using the above mentioned wet method to find the optimum conditions regarding calcination time, sintering time and temperature and Pb substitution so that the volume fraction of 2223 phase can be maximised.

The best preparation conditions have been fixed on the basis of temperature-resistivity ($T_r$) and critical current density ($J_c$) measurements whereas the X-ray diffraction (XRD), Energy dispersive X-ray analysis (EDX) and Scanning electron microscopy (SEM) observations have been used to correlate the changes in superconducting properties with the sample microstructure. Finally, the stability of the various superconducting phases under simulated conditions of long hours of exposure to moist atmosphere has been tested.

2. Experimental

Different aqueous solutions were prepared by dissolving the appropriate amounts of Bi(NO$_3$)$_3$.5H$_2$O: Pb(NO$_3$)$_2$: Sr(NO$_3$)$_2$: Ca(NO$_3$)$_2$.4H$_2$O: Cu(NO$_3$)$_2$.3H$_2$O (each chemical 99.9 % pure) in de-ionised water with a small amount of nitric acid [4]. The atomic ratios of Bi : Pb : Sr : Ca : Cu in the above solution were $(2.2 - x): x : 2 : 2.3 : 3.5$ with $x = 0.4$ and 0.5. The solution was evaporated to dryness, calcined in air at 810°C for (a) 12 hours for
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some samples and (b) twice for 20 and 4 hours successively for other samples, with regrinding in between. The powder was sintered in air at different temperatures between 840°C and 860°C for different durations i.e., 72 hours to 175 hours [5,6] in a programmable furnace (Thermolyne Type 54500) and subsequently furnace cooled. The standard four probe technique was used for electrical resistivity measurements in order to determine the critical temperature $T_c$ and critical current density $J_c$. A programmable current source (224 Keithley), a nanovoltmeter (181 Keithley) and a closed cycle Cryocooler (8001 Controller with 8300 Compressor RMC USA) have been used for this purpose. For all these measurements the conventional 1 $\mu$V/cm criterion was used.

The XRD pattern was observed using CuK$_\alpha$ radiation on a Philips (PW 1050,51) X-ray diffractometer whereas the microstructure was examined in a SEM (S-2300 Hitachi) and the composition investigated using EDX.

For the measurements of stability of the samples, prepared under different conditions, they were suspended together in an enclosure containing saturated water vapour and their $T_c$ and $J_c$ were measured at regular intervals over a period of 10 days.

3. Results and discussion

Altogether nine samples were prepared varying Pb content, calcination time, sintering time and temperature. They all (except SC1 and SC2) show Meissner effect at liquid nitrogen temperature. The experimental results are discussed below in detail.

3.1. Variation of $T_c$ as a function of the calcination time, sintering time and sintering temperature:

The onset and zero resistance $T_c$'s observed for different samples prepared by varying calcination time and sintering time and temperature are given in Table 1. It may be pointed out

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Pb content X value</th>
<th>Calcined for</th>
<th>Sintered for</th>
<th>$T_c$ in °K</th>
<th>$R = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>time in hrs.</td>
<td>temp in °C</td>
<td>time in hrs.</td>
<td>temp in °C</td>
</tr>
<tr>
<td>SC1</td>
<td>0.4</td>
<td>20+4</td>
<td>810</td>
<td>72</td>
<td>850</td>
</tr>
<tr>
<td>SC2</td>
<td>0.5</td>
<td>12</td>
<td>810</td>
<td>72</td>
<td>850</td>
</tr>
<tr>
<td>SC3</td>
<td>0.5</td>
<td>20+4</td>
<td>810</td>
<td>840</td>
<td>120</td>
</tr>
<tr>
<td>SC4</td>
<td></td>
<td></td>
<td></td>
<td>72</td>
<td>850</td>
</tr>
<tr>
<td>SC5</td>
<td>0.5</td>
<td></td>
<td></td>
<td>860</td>
<td>110</td>
</tr>
<tr>
<td>SC6</td>
<td></td>
<td></td>
<td></td>
<td>90</td>
<td>850</td>
</tr>
<tr>
<td>SC7</td>
<td></td>
<td></td>
<td></td>
<td>850</td>
<td>120</td>
</tr>
<tr>
<td>SC8</td>
<td></td>
<td></td>
<td></td>
<td>850</td>
<td>120</td>
</tr>
<tr>
<td>SC9</td>
<td></td>
<td></td>
<td></td>
<td>850</td>
<td>120</td>
</tr>
</tbody>
</table>
that detailed experiments were not performed on samples with higher proportions of Pb than $x = 0.5$ since preliminary results obtained by us and also by previous workers [3] indicated that superconducting properties drastically deteriorated under these conditions.

From the table it is evident that $T_c$ depends strongly on the calcination and sintering conditions and the doping percentage of Pb.

The variation of resistance with temperature for samples with Pb content $x = 0.4$ has been shown in Figure 1. On comparing the resistance data of the samples SC1 and SC2, it is seen that $T_c (R = 0)$ decreases on increasing the sintering time from 72 to 90 hours. This point will be further clarified when Figure 2a where Pb content is $x = 0.5$ is considered.

Comparing the resistance curves of SC6, SC8 and SC9 (Figure 2a) where sintering time has been increased from 72 to 110 hours progressively from sample to sample keeping other parameters like calcination time and sintering temperature (i.e., 850°C) same, it is seen that 90 hours seems to be the best sintering time (sample SC8) because the corresponding $T_c$ (onset) and $T_c$ (zero) are the highest. Similarly, comparing the curves of SC5, SC6 and SC7 (Figure 2b) where sintering temperature only has been changed from 840 to 860°C, it is evident that 850°C is the best sintering temperature. $T_c$ also depends on calcination time. The sample SC6 calcined twice for 20 hours and 4 hours with grinding in between has a higher $T_c$ than the sample SC3 calcined for 12 hours at the same temperature (Figure 2c).

Thus from the above results, it is clear that in order to produce the sample with the highest $T_c (R = 0)$ (no. SC8), it is necessary to calcine twice at 810°C for 24 hours with grinding in between, followed by sintering at 850°C for 90 hours. $T_c$ was found to decrease on changing either the calcination time, sintering temperature or its duration. Lower $T_c$ values for samples sintered at higher temperatures or for longer durations may be due to the
decomposition of the 2223 phase into other non-superconducting oxides. Further, under these conditions, lead concentration probably decreases causing degradation of $T_c$. On the other hand, when the sample was sintered for shorter durations or at lower temperatures, $T_c (R = 0)$ was lowered, probably on account of the incomplete growth of the 2223 phase.

3.2. $J_c$ measurements:

$J_c$ measurements have been performed at 77 K on samples no. SC8 and SC9 and at 60 K on sample no. SC2. The sample with the highest $T_c (R = 0)$, also gives the best $J_c$ (~ 300 A/cm²). This is in agreement with the finding of Maeda et al [8]. $J_c$ for the samples SC2 and SC9 is measured to be ~ 2 A/cm² and ~ 45 A/cm² respectively.

3.3. XRD studies:

In order to elucidate the structural part, XRD studies have been done in detail on samples having Pb content $x = 0.5$ because these samples possess relatively higher $T_c (R=0)$ values than others. On comparing the X-ray diffractogram of samples SC2 and SC8 (Figures 3b and 4f) which are treated under the same conditions, it is clear that in the latter sample with Pb content $x = 0.5$, the relative intensities of the peaks corresponding to the 2223 phase are larger than the former containing Pb content $x = 0.4$. It is also important to note that the intensities of prominent peaks of the 2212 phase decrease sharply as the percentage of lead is increased. There is also an observable decrease in the concentration of impurities. The XRD patterns of samples SC6 (Figure 4d) and SC8 (Figure 4f), which only differ on sintering.
time, are more or less similar except that the 2223 peaks are more intense and the 2212 peaks weaker in the latter case. This is also true for samples SC1 and SC2 (Figures 3a and 3b)

Figure 3. XRD patterns of \(\text{Bi}_{2.2} \text{Sr}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_{y}\) with Pb content \(x = 0.4\) sintered at (a) 850°C for 72 hrs after being calcined for 24 hrs (SC1). (b) 850°C for 90 hrs after being calcined for 24 hrs (SC2).

\(\Delta - 2223, \Box - 2212, \triangle - 2201, \bullet - \text{Impurities (Bi}_2\text{O}_3, \text{Ca}_2\text{PbO}_4, \text{CuO etc.)}\)

with Pb content 0.4. It is well known that prolonged sintering is also detrimental to the superconducting properties and to bring this point into focus, we have prepared samples SC3 and SC4 under identical conditions, except that in the former case the sintering time is 72 hours and in the latter 175 hours. The respective XRD patterns (Figures 4a and 4b) clearly reveal that prolonged sintering decomposes the 2223 phase into the 2212 phase with a resultant fall in \(T_c\) (Table 1). Thus there exists an optimum duration of the sintering process, on either side of which \(T_c\) decreases.

It is also to be noted that the XRD pattern for the sample SC5 (Figure 4c) sintered at 840°C, contains more of the peaks of the 2212 phase and less of the 2223 phase compared to the sample SC6 (Figure 4d) sintered at 850°C. The sample SC7 (Figure 4e), sintered at 860°C for 72 hours, also shows a lower proportion of the peaks of the 2223 phase. That the sample SC6 possesses the highest \(T_c\) \((R = 0)\) value among these three samples, is compatible with the X-ray data. Thus, there exists an optimum sintering temperature (in this case 850°C) for obtaining the maximum proportion of the higher \(T_c\) (2223) phase. Thus, this study indicates that the sample SC8 (Figure 4f) appears to have the best sintering conditions (sintering at 850°C for 90 hours), as far as the superconducting transition temperature (both the onset and zero resistance values) is concerned. In this case the 2223 phase is most well developed at the expense of the 2212 phase.

Thus, the XRD study gives us an insight into what is actually happening under different preparation conditions and leads us to conclude that it is the concentration of the 2223 phase that is responsible for the improvement of superconducting properties. The
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Relative increase of $T_c$, be it by changing the calcination or the sintering conditions (Table 1), could always be linked, from the XRD analysis, to an increase in volume fraction or the 2223 phase. This quantity can be roughly estimated by the ratio of $I_A(2223) / (I_A(2223) + I_{(2212)})$, where the $I_A(2223)$ is the intensity of the strongest peak for the 2223 phase and

**Figure 4.** XRD patterns of (Bi$_{2-y}$Pb$_y$)$_2$.Sr$_2$.Ca$_{y+2}$.Cu$_{y+3}$.O$_{10+y}$ with Pb content ($y = 0.5$) sintered at (a) 850°C for 72 hrs after being calcined for 12 hrs (SC3). (b) 850°C for 175 hrs after being calcined for 12 hrs (SC4). (c) 840°C for 72 hrs after being calcined for 24 hrs (SC5). (d) 850°C for 72 hrs after being calcined for 24 hrs (SC6). (e) 860°C for 72 hrs after being calcined for 24 hrs (SC7). (f) 850°C for 90 hrs after being calcined for 24 hrs (SC8).

$\Delta$ - 2223, $\bigcirc$ - 2212, $\Delta$ - 2201, $\bullet$ - Impurities (Bi$_2$O$_3$, Ca$_2$PbO$_4$, CuO etc.)

$I_A(2212)$ is the same for the 2212 phase [9]. The volume fraction of the 2223 phase for the sample which shows the best $T_c$ ($R = 0$), viz. SC8, is found to be 76.8% whereas the same for the sample which shows the lowest $T_c$ ($R = 0$), viz. SC2 is found to be 57.5%. Also from the analysis of XRD pattern, the lattice parameters obtained for the two phases 2212 and 2223 are $a = b = 5.39$ Å and $c = 30.83$ Å and 37.33 Å respectively, which are very close to earlier quoted values in the literature [2,10].
3.4. EDX analysis:

EDX analysis has been performed for three samples: SC2, SC8 and SC9, in order to estimate the ratio of Ca : Cu. Three different regions from each sample have been chosen. For the sample SC8 which shows the best \( T_c \) (zero resistance) of 111 K, the Ca : Cu ratio is found to be 0.66. The corresponding values for the other two samples (no. SC2 and SC9) are about 0.5. This indicates the predominance of 2223 phase in the sample SC8 over other samples.

3.5. Stability of the high \( T_c \) phase:

We have also tested the stability of the three samples SC2, SC8 and SC9 in aqueous vapour. High \( T_c \) superconductors are known to be very susceptible to moisture and their superconducting properties degrade as a general rule. In order to simulate long hours of degradation under moist atmospheric conditions, we suspended the three samples in an enclosure containing saturated aqueous vapour for 10 days. No sharp deterioration in the superconducting transition temperature was observed, although \( J_c \) was found to decrease by more than one order of magnitude for the sample with the highest \( T_c \) and \( J_c \) (SC8). The sample with the lowest \( T_c \) and \( J_c \) (SC2) remained largely unaffected, while the effect of sample SC9 was found to be intermediate between the two. The results of our \( T_c \) and \( J_c \) measurements both immediately after production and after the above degradation treatments are summarised in Table 2.

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Composition</th>
<th>Immediately after Production</th>
<th>After degradation treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( T_c ) onset (zero)</td>
<td>( J_c ) in A/cm²</td>
</tr>
<tr>
<td>SC2</td>
<td>( X = 0.4 )</td>
<td>100 72 -2</td>
<td>98 70 -2</td>
</tr>
<tr>
<td>SC8</td>
<td>( X = 0.5 )</td>
<td>150 111 -300</td>
<td>142 103 -10</td>
</tr>
<tr>
<td>SC9</td>
<td>( X = 0.5 )</td>
<td>120 95 -45</td>
<td>120 93 -9</td>
</tr>
</tbody>
</table>

3.6. Microstructure analysis by SEM:

The SEM micrographs of the fractured surface for samples with different lead contents and sintering times have been shown in Figure 5. The sample with Pb content, \( x = 0.5 \) sintered at 850°C for 90 hours (SC8) shows large cylindrical grain growth (Figure 5a). When the same sample is sintered for 110 hours (SC9), we find that the cylindrical grain formation is destroyed (Figure 5b). Figure 5c represents the SEM micrograph for the sample with
Figure 5. SEM micrographs of \((\text{Bi}_{2.2-x}\text{Pb}_x\text{Sr}_3\text{Ca}_2\text{Cu}_3\text{O}_y)\) with Pb content (a) \(x = 0.5\), sintered at 850°C for 90 hrs (SC8). (b) \(x = 0.5\), sintered at 850°C for 110 hrs (SC9)
Figure 5. SEM micrographs of \((\text{Bi}_{2.2}, \text{Pb}_{1})\text{Sr}_{2}\text{Ca}_{2}\text{Cu}_{1.5}\text{O}_{y}\) with \(\text{Pb}\) content (c) sintered at 850°C for 90 hrs (SC2).
lead content, $x = 0.4$, sintered at $850^\circ C$ for 90 hours (SC2). This shows a floral structure and randomly oriented grains. From the resistivity measurements and XRD and EDX analyses, it seems that the large cylindrical grain growth is characteristic of the high-$T_c$ (2223) phase and the floral structure that of the low-$T_c$ (2212) phase. Similar grain growth has also been observed by Yoon and Lee [6]. Figure 5b probably represents incomplete transition from the former to the latter which is in agreement with the XRD observation, implying that the high-$T_c$ (2223) phase decomposes into the low-$T_c$ (2212) phase on prolonged sintering.

The observed microstructure can now be correlated to the $T_c$ and $J_c$ values observed immediately after production, and after long hours of treatment in humid atmosphere. Sample SC8 (Figure 5a) has prominent grain boundaries along which oxygen can be channelised, ensuring uniform oxidation throughout the bulk. It results in a superconductor with both high $T_c$ and $J_c$ (Table 2). However, it is also expected that moisture or any other impurity responsible for degradation of superconducting properties would also easily creep through the same path, so that this sample is also expected to be most vulnerable to degradation due to weak link formation along these boundaries. Sample SC2 on the other hand consists of randomly oriented grains, into the bulk of which, it would be difficult for oxygen to reach uniformly. This material, therefore, is likely to be more oxygen deficient than desired, resulting in lower $T_c$ and $J_c$ immediately after production. The absence of channelised paths however is responsible for the degradation of this material at a slower rate, and this is borne out by our experimental measurements (Table 2). SC9 represents a mixture of the two states. It may be pointed out that similar conclusions have also been made by Y-Ba-Cu-O group of high-$T_c$ and superconductors [11].

4. Conclusion

In this paper, our main aim was to achieve the best preparation conditions of the Bi(Pb)-Sr-Ca-Cu-O group of high-$T_c$ compounds in order to obtain a compound that contains the highest percentage of the high-$T_c$ (2223) phase. Incidentally, the sample prepared by us has one of the highest $T_c (R = 0)$ obtained by this method. Although it was not possible to isolate this phase completely by this procedure, the sample SC8 was found to contain a very high proportion of it, as is evident from the XRD and EDX analyses. Our experiments further revealed that the sample SC8 with the highest $T_c$ also yielded the highest $J_c$. However, it was also found to be most susceptible to degradation (Table 2), and the critical current density, in particular, decreases by more than an order of magnitude. The microstructure analysis could correlate this degradation to the inherent characteristics of the as-produced sample. The well defined grain boundaries of the sample SC8 (Figure 5a), while providing convenient paths for uniform oxidation of the material (resulting in high $T_c$ and $J_c$ ), also served as possible superconducting weak links on long exposure to moist atmosphere. This then is a serious drawback from the point of view of applicability of such a material in large current producing devices. On the other hand, although the sample SC2 is very stable, its inherent low $J_c$ value
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(Table 2) also does not make it very attractive in a superconducting device. We conclude that
suitable tailoring and patterning must be introduced during the actual synthesis of the material
in order to obtain a sample that will not only have both high $T_c$ and $J_c$ but will also be fairly
resistant to degradation and that optimisation should relate not only to the isolation of a high-
$T_c$ phase, but also to the suitability of the material produced for device applications.

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