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Variation of structural and superconducting properties with initial stoichiometry variation in (Bi,Pb)–Sr–Ca–Cu–O bulk superconductor

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The effect of the initial stoichiometry variation (variation in Bi, Pb, Sr, Ca and Cu) on various structural and superconducting properties of Pb-doped Bi-based superconductor has been studied. The sample having the initial stoichiometry of $(Bi_{1.8}Pb_{0.4})Sr_2Ca_{2.2}Cu_3O_{10}$ was found to give best structural and superconducting properties. The most important factors affecting J_c in the samples were the type of impurity phases present in the sample, their amount and distribution in the superconducting matrix. Cu-rich stoichiometry enhanced the formation of 110 K phase, but large amounts of undesirable impurities present in the samples decreased J_c. The formation of 110 K phase and texturing of (0 0 l) planes in a sample depended on the period of heat treatment and stoichiometry.

1. Introduction

It is well known that the two important superconducting phases in the Bi–Sr–Ca–Cu–O system are $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (2212 phase), with $T_c \sim 85$ K, and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223 phase), with $T_c \sim 110$ K. It has also been found, from phase equilibria studies in the quaternary system Bi_2O_3–SrO–CaO–CuO [1], that the 2212 phase is thermodynamically stable over a wide range temperature and in the presence of most of the compounds existing in this system. In contrast, the 2223 phase is stable only over a narrow temperature range and exhibits phase equilibria with fewer compounds existing in the system. Therefore, the synthesis of a pure 2223 phase is more difficult than the synthesis of a 2212 phase. At the same time, it has been established that the partial substitution of Bi by Pb favours the formation of the 2223 phase [2]. The structural and superconducting properties of Pb-doped Bi-based superconductor has been found to depend both on the initial stoichiometry and processing conditions [3–6]. Thus, the study of the effect of initial stoichiometric variation and processing conditions on the structural and superconducting properties of this system is of great significance.

In the present investigation (Bi,Pb)–Sr–Ca–Cu–O samples having different initial stoichiometries (variation in Bi, Pb, Sr, Ca and Cu) were synthesized by a conventional ceramic route in air. Changes in various structural and superconducting parameters, such as high T_c (2223 phase) fraction (HTf), low T_c (2212 phase) fraction (LTf), impurity fraction (If), texturing of (0 0 l) planes (T_{00l}), $T_c(0)$, ΔT_c, J_c, $J_c(B)$, etc., of the samples, with respect to the different initial stoichiometries and soaking periods, were studied. Also, an attempt was made to differentiate the major impurity phases depending on whether they enhanced the J_c or not.

2. Experimental procedure

Samples having initial stoichiometries $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$, $Bi_{1.6+x}Pb_{0.4}Sr_2Ca_2Cu_3O_y$, $Bi_{1.8}Pb_{0.4}Sr_{2\pm x}Ca_2Cu_3O_y$, $Bi_{1.8}Pb_{0.4}Sr_2Ca_{2\pm x}Cu_3O_y$, $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_{3\pm x}O_y$ (where $x = 0$–0.6) were prepared as follows. Stoichiometric amounts of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO (Aldrich, 99.9% pure) were well mixed in an agate mortar and calcined at 800 °C in air for 12 h and at 845 °C for 120 h. The samples were then ground and bar-shaped specimens (20 × 4 × 2 mm) were prepared. The bars were sintered in air at 848 °C for 80 h. X-ray diffraction (XRD) experiments were performed on Philips PW 1710 powder diffractometer using CuK_α-radiation under identical conditions. The critical temperatures of the samples were measured by a standard four-probe d.c. technique, using an APD cryostat. The direct transport method was used to determine the critical current density of the sample. $J_c(B)$ characteristics were measured at liquid nitrogen temperature by placing the sample axially at the centre of an electromagnetic coil.

In the course of present investigation a simple method is suggested by which a semi-quantitative estimation of HTf, LTf and If, as well as T_{00l} [hereafter these parameters are referred to as PS (phase and structural) parameters] can be made from XRD patterns of the samples. The basic assumption in the method suggested here is that each phase, namely high T_c, low T_c and major impurities (semiconducting

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($2\theta = 21.9°$) [7], and Ca_2PbO_4 ($2\theta = 17.8°$) compounds) have their own characteristic X-ray reflections at different angles. Further, from the XRD patterns of the samples, it was found that two types of planes, namely (0 0 l) and (1 1 l) grew preferentially during the processing period. Texturing of the (0 0 l) plane was desirable because of its increased capacity of critical current density [8].

For the determination of HTf, LTf and If, XRD patterns were taken after grinding the samples for about 0.5 h and then sieving. These samples were filled in a sample holder, following a standard method [9], to avoid texturing due to sample preparation. All other experimental parameters were kept identical. Integrated intensities of two XRD lines were chosen for each phase such that they had minimum overlap and higher intensities. For the determination of $T_{0 0 1}$ of the sintered sample, XRD was performed at different depths in the sample, under identical conditions.

The PS parameters were defined as follows, where HTf + LTf + If = 1.

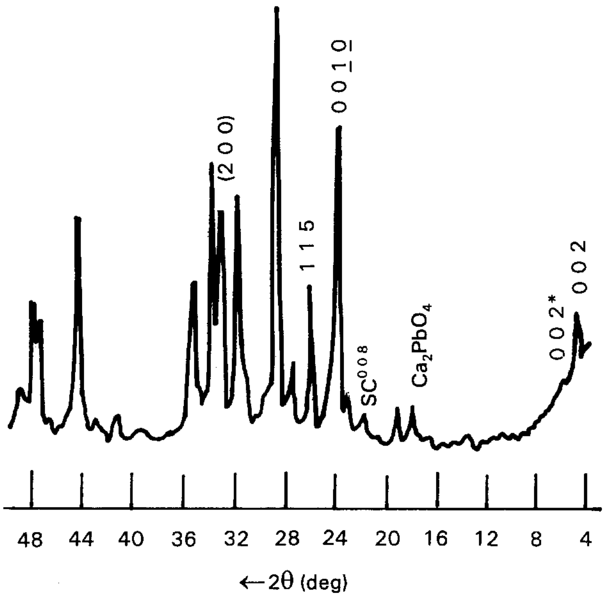

Figure 1 Typical XRD pattern of (Bi,Pb)Sr, Ca, Cu, O.

$$\mathrm{HTf} = \frac{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°)}{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°) + I^*_{0 0 2}(5.8°) + I^*_{0 0 8}(23.2°) + I_{\mathrm{imp}}(17.8°) + I_{\mathrm{imp}}(21.9°)}$$

$$\mathrm{LTf} = \frac{I^*_{0 0 2}(5.8°) + I^*_{0 0 8}(23.2°)}{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°) + I^*_{0 0 2}(5.8°) + I^*_{0 0 8}(23.2°) + I_{\mathrm{imp}}(17.8°) + I_{\mathrm{imp}}(21.9°)}$$

$$\mathrm{If} = \frac{I_{\mathrm{imp}}(17.8°) + I_{\mathrm{imp}}(21.9°)}{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°) + I^*_{0 0 2}(5.8°) + I^*_{0 0 8}(23.2°) + I_{\mathrm{imp}}(17.8°) + I_{\mathrm{imp}}(21.9°)}$$

$$T_{0 0 1} = \frac{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°)}{I_{0 0 2}(4.7°) + I_{0 0 \underline{10}}(23.9°) + I_{1 1 5}(26.2°) + I_{2 0 0}(33.2°)}$$

where I and I^* refer to the integrated intensity of the peaks corresponding to the 2223 and 2212 phases, respectively, and I_{imp} the intensity of impurity peak. The above reflections are marked in the typical XRD pattern given in Fig. 1.

3. Results and discussion

3.1. Effect of Pb doping

Samples having different Bi:Pb stoichiometric ratios have been prepared and various structural and superconducting properties studied to select the best combination. The different PS parameters, T_c, ΔT_c and J_c, of the samples after 120 + 80 h of heat-treatment are shown in Tables I and II.

From Tables I and II, Bi:Pb the stoichiometric ratio 1.8:0.4 was found to give the best PS parameters and superconducting properties. Therefore, in the experiments varying Sr, Ca and Cu stoichiometries the Bi:Pb molar ratio was kept at 1.8:0.4.

3.2. Effect of Sr, Ca and Cu variations

Figs 2 and 3 show the variation of HTf, If, $T_{0 0 1}$, T_c, ΔT_c and J_c of the 120 + 80 h heat treated samples with x. From the figures it can be seen that the samples

TABLE I Different PS parameters, T_c, ΔT_c and J_c of the samples having different Bi:Pb stoichiometric ratios, after 120 + 80 h of heat-treatment

Bi:Pb	HTf	LTf	If	$T_{0 0 1}$	$T_c(0)$ (*K*)	ΔT_c (K)	J_c (A cm^{-2})
1.9:0.1	0.6481	0.2969	0.055	0.3888	105	7	120
1.8:0.2	0.7655	0.1935	0.041	0.4551	107	5	162
1.7:0.3	0.90	0.065	0.035	0.5663	109	4	223
1.6:0.4	0.91	0.063	0.027	0.75	109	4	252
1.5:0.5	0.741	0.211	0.048	0.542	107	6	148
1.4:0.6	0.621	0.34	0.65	0.3443	104	8	105

TABLE II Different PS parameters, T_c, ΔT_c and J_c of the samples having stoichiometries $\mathrm{Bi}_{1.6+x}\mathrm{Pb}_{0.4}\mathrm{Sr}_2\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_{10}$ after 120 + 80 h of heat-treatment

Bi:Pb	HTf	LTf	If	T_{001}	$T_c(0)$ (K)	ΔT_c (K)	J_c (A cm^{-2})
1.6:4	0.91	0.063	0.027	0.75	109	4	252
1.7:4	0.917	0.061	0.022	0.75	109	4	267
1.8:4	0.92	0.06	0.02	0.76	109	4	312
1.9:4	0.90	0.068	0.04	0.73	107	6	149

Note: Since samples of $x > 0.3$ showed no improvement in superconducting and structural properties they are not given in the table.

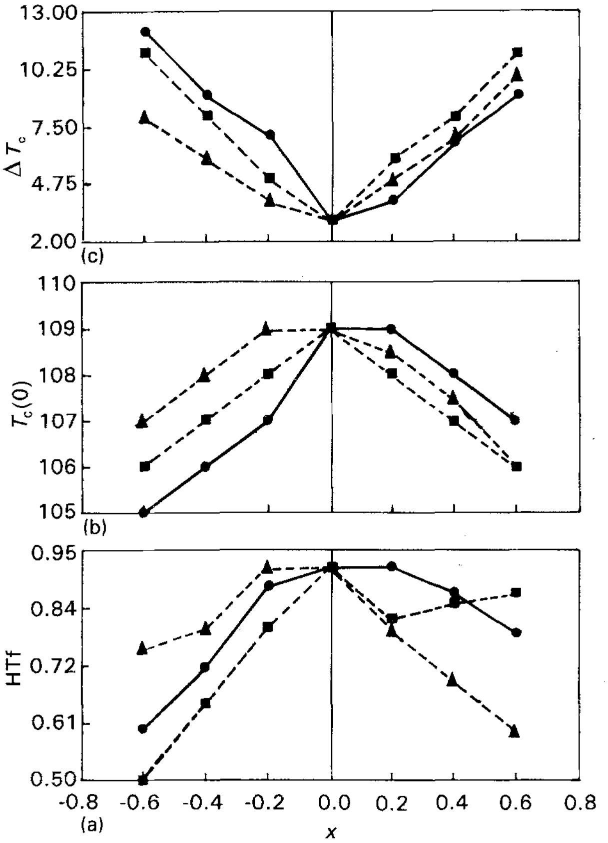

Figure 2 Plots of (a) HTf, (b) $T_c(0)$ and (c) ΔT_c versus x. Variation in: —●—, Ca; – – ▲ – –, Sr; – – ■ – –, Cu.

which had the initial stoichiometries showed the best properties, i.e. highest T_c, lower ΔT_c and higher J_c.

1. $\mathrm{Bi}_{1.8}\mathrm{Pb}_{0.4}\mathrm{Sr}_{1.8}\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_y$ (sample 1)
2. $\mathrm{Bi}_{1.8}\mathrm{Pb}_{0.4}\mathrm{Sr}_2\mathrm{Ca}_{2.2}\mathrm{Cu}_3\mathrm{O}_y$ (sample 2)
3. $\mathrm{Bi}_{1.8}\mathrm{Pb}_{0.4}\mathrm{Sr}_2\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_y$ (sample 3)

In order to study the combined effect of stoichimetries of samples 1–3, a sample of $\mathrm{Bi}_{1.8}\mathrm{Pb}_{0.4}\mathrm{Sr}_{1.8}\mathrm{Ca}_{2.2}\mathrm{Cu}_3\mathrm{O}_y$ was prepared and its PS parameters, T_c, ΔT_c and J_c were determined; Table III shows the results. None of the values were better than those of samples 1–3.

3.3. Effect of impurity phases on J_c

Sample 2 exhibited a sharp increase in J_c (Fig. 3a), but there was no significant increase in the texturing of the (001) planes (Fig. 3c) or HTf (Fig. 2a), compared to samples 1 and 3.

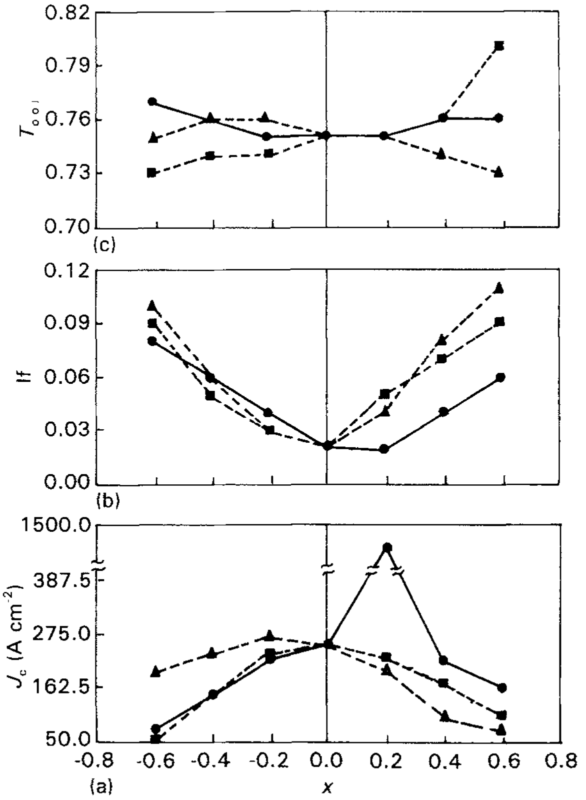

Figure 3 Plots of (a) J_c, (b) If and (c) T_{001} versus x. Variation in: —●—, Ca; – – ▲ – –, Sr; – – ■ – –, Cu.

TABLE III PS parameters, T_c, ΔT_c and J_c of the sample having the initial stoichiometry $\mathrm{Bi}_{1.8}\mathrm{Pb}_{0.4}\mathrm{Sr}_{1.8}\mathrm{Ca}_{2.2}\mathrm{Cu}_3\mathrm{O}_y$

HTf	LTf	If	T_{001}	$T_c(0)$ (K)	ΔT_c (K)	J_c (A cm^{-2})
0.854	0.112	0.034	0.74	108	6	215

The impurity phases used in the present definition of If were the $\mathrm{Ca}_2\mathrm{PbO}_4$ and the semiconducting phase. The dependence of J_c on this factor can be seen by comparing the J_c values (Fig. 3a) with the If (Fig. 3b) values. The general trend is a decreasing J_c and an increasing If going away from the 2223 stoichiometric initial composition. But the abrupt increase and fall of J_c on following the excess Ca regime is worthy of mention. A closer look at the XRD patterns (Fig. 4) at a higher scale factor for excess Ca stoichiometries revealed the presence of $\mathrm{Ca}_2\mathrm{CuO}_3$ ($2\theta = 36.7°$) as an additional phase for all these compositions. Also, the

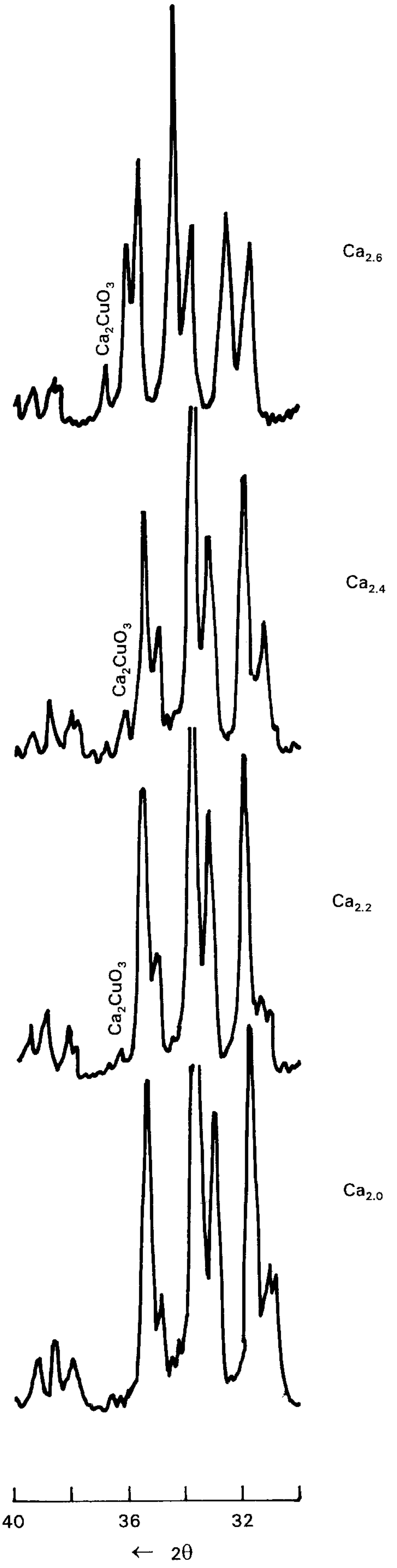

Figure 4 XRD patterns of different Ca stoichiometric samples.

Figure 5 SEM fractograph of the sample having Ca stoichiometry of 2.2.

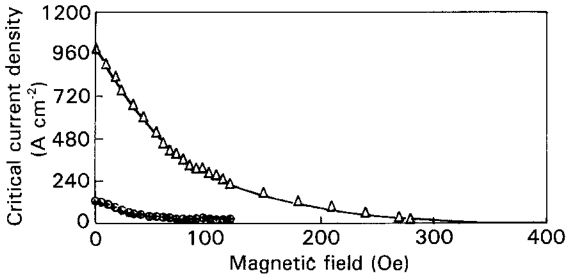

Figure 6 J_c(B) characteristics of samples 1 (+), 2 (Δ) and 3 (○).

amount of this phase was found to increase as the Ca content increased. The SEM photograph (Fig. 5) of this sample taken at a magnification of × 6000 shows distribution of fine precipitates (which were absent in other compositions) in the superconducting matrix. These precipitates may have been Ca$_2$CuO$_3$. It has been reported that Ca$_2$CuO$_3$ can act as a flux pinning centre [10]. Also J_c(B) characteristics of samples 1–3 (Fig. 6) show that sample 2 also had an improved magnetic performance. Therefore, the increase in J_c in Ca$_{2.2}$ stoichiometric samples may have been due to the flux pinning action of finely distributed Ca$_2$CuO$_3$ present. However, increasing the amount of Ca$_2$CuO$_3$ in samples with Ca stoichiometries of more than 2.2 did not seem to increase J_c. This may have been due to the following reasons:

1. the amount of Ca$_2$CuO$_3$ present in these samples may have been higher than that required for the flux pinning action, and hence it acted as an impurity phase just like other impurity phases;
2. from the Fig. 3b it can be seen that the impurity level was significantly higher in samples with a Ca stoichiometry higher than 2.2.

3.4. Best initial stoichiometry

From these studies, it was found that Bi$_{1.8}$Pb$_{0.4}$-Sr$_2$Ca$_{2.2}$Cu$_3$O$_y$ was the best initial stoichiometry, giving higher T_c, J_c and better J_c(B) characteristics.

3.5. Effect of soaking period on HTf

Fig. 7 shows the variation of HTf with x after 120 and 120 + 80 h of heat-treatment. In all cases HTf increased with an increasing period of heat-treatment.

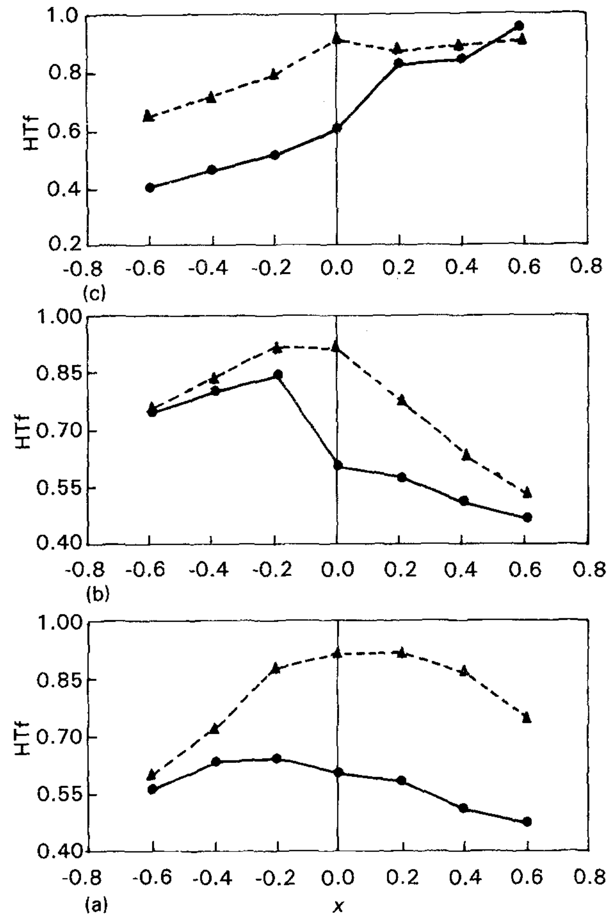

Figure 7 Plots of HTf versus x for different stoichiometric samples after 120 (—●—) and 120 + 80 h (– – ▲ – –) of heat treatment. Variation in: (a) Ca; (b) Sr; and (c) Cu.

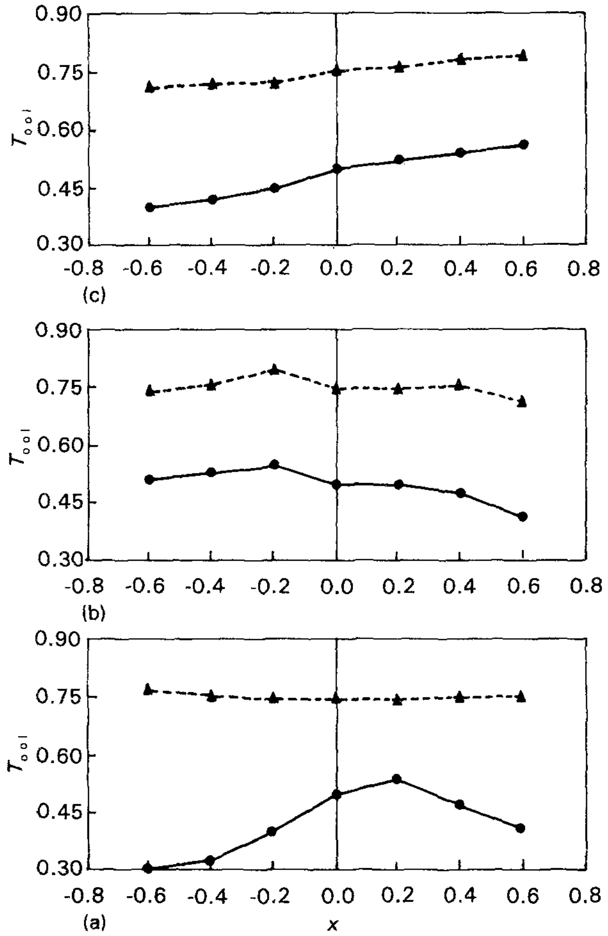

Figure 8 Plots of T_{001} versus x of different stoichiometric samples after 120 (—●—) and 120 + 80 h (– – ▲ – –) of heat-treatment. Variation in: (a) Ca; (b) Sr; and (c) Cu.

TABLE IV HTf and T_{001} corresponding to 120 and 120 + 80 h heat-treated Cu-rich stoichiometric samples

Cu stoichiometry	$HTf_{(120)}$	$T_{001\,(120)}$	$HTf_{(120+80)}$	$T_{001(120+80)}$
3.0	0.64	0.38	0.92	0.75
3.2	0.75	0.33	0.82	0.75
3.4	0.8	0.42	0.84	0.75
3.6	0.89	0.53	0.87	0.79

But, in the case of Cu-rich stoichiometry ($\geq Cu_{3.4}$), 80–90% HTf was attained within 120 h of heat-treatment. However, after 120 h there was no further significant increase in HTf in these samples.

3.6. Effect of soaking period on T_{001}

Fig. 8 shows the variation in texturing of (0 0 1) planes with x after 120 and 120 + 80 h heat-treatment. Texturing of (0 0 1) planes also increased with an increase in the period of heat-treatment for all stoichiometries. Another factor improving the texturing was a Cu-rich stoichiometry (Fig. 3c). But, increasing in T_{001} by Cu-rich stoichiometry did not improve the J_c value of the sample (Fig. 3a). This may have been because of the higher amounts of impurity phases present in the sample (Fig. 3b).

Table IV gives the HTf and T_{001} corresponding to 120 and 120 + 80 h heat-treated Cu-rich stoichiometric samples. From the table it is clear that in the case of Cu-rich stoichiometric samples, even though HTf (120 h) was comparable with HTf (120 + 80 h), T_{001}(120 h) was much lower than T_{001} (120 + 80 h). Thus, the formation of the 2223 phase could be accelerated by a Cu-rich liquid-phase reaction, but for higher texturing, a sufficient soaking period was needed.

4. Conclusions

The effect of the initial stoichiometry variation (variation in Bi, Pb, Sr, Ca and Cu) on various structural and superconducting properties of the Pb-doped Bi-based superconductor has been studied. From the studies the following conclusions can be drawn:

1. The sample having initial stoichiometry $Bi_{1.8}Pb_{0.4}Sr_2Ca_{2.2}Cu_3O_y$ gives the best structural

and superconducting properties. It has been found that the most important factors affecting J_c in this sample are the type of impurity phases present, their amount and their distribution in the superconducting matrix.

2. Cu-rich stoichiometry enhances the formation of 110 K phase by Cu-rich liquid-phase reaction, but the large amount of impurities present in the sample decreased J_c.
3. The formation of 110 K phase and texturing of (0 0 l) planes in a (Bi, Pb)–Sr–Ca–Cu–O sample depended on the period of heat-treatment and stoichiometry.

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