

Preparation and degradation behaviour of Bi-cuprate superconductors

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Abstract. The role of preparation conditions and the effect of addition of Pb in Bi-Sr-Ca-Cu-O (BSCCO) superconductor, on the T_c , J_c and grain orientation have been studied. Calcination at a temperature higher than the melting point of Bi_2O_3 after the prereaction at 800°C leads to formation of c -axis oriented nearly single phase material. The presence of lead yields a nearly high T_c phase (2223) exhibiting a maximum transition temperature $T_c = 110\text{ K}$ and $\Delta T_c = 2\text{ K}$. The addition of lead and grain orientation together result in an increase in J_c by nearly two orders of magnitude. The degradation behaviour was studied in terms of changes in T_c , J_c and structure on exposure to atmosphere up to 250 days. Samples with 0.6 Pb were found to be superconducting with $T_c = 97\text{ K}$ even after 250 days. The high T_c phase was stable against degradation. Our studies indicate that the degradation of leaded BSCCO is a surface phenomenon rather than bulk phenomenon.

Keywords. High temperature superconductors; leaded BSCCO superconductors; c -axis orientation; degradation behaviour.

1. Introduction

The discovery of Bi- (Michel *et al* 1987; Maeda *et al* 1988) and Tl- (Sheng and Hermann 1988) cuprate superconductors has attracted the attention of many research groups due to their higher zero resistance temperature, $T_c(R=0)$ or simply T_c . The Bi-cuprate system, in general, has three different phases corresponding to T_c close to 20, 80 and 110 K. Numerous studies have been made to synthesize and stabilize the pure high T_c (110 K) phase by varying the processing parameters like cation non-stoichiometry (Koyama *et al* 1988), heat treatment conditions (Tarascon *et al* 1988), cooling rate (Kikuchi *et al* 1989) and by the addition of Pb (Sunshine *et al* 1988; Statt *et al* 1988) to the Bi-Sr-Ca-Cu-O (BSCCO) system. However, the highest value of T_c was achieved only when sintering was done for long durations (Chavira *et al* 1988; Kim *et al* 1989) up to 200-300 hr. Besides, critical current density, J_c , of these materials is still very low as compared to the YBCO superconductor. One of the reasons is the random growth of the plate-like grains of the high T_c phase.

The BSCCO superconductors need to be densified and the grains oriented so that their J_c is increased. Some special techniques like intermediate cold pressing (Asano *et al* 1988; Ito 1989), hot pressing (Murayama *et al* 1988), low oxygen partial pressure during sintering (Endo *et al* 1988) etc. have been tried to obtain c -axis oriented samples having higher J_c . These techniques are, however, quite elaborate and complicate the processing steps. We have tried to achieve the same by simply changing the reaction process conditions.

The conversion of 2223 phase into low T_c phase is one of the major problems of environmental stability thus lowering the T_c and J_c . We have studied this stability in the bulk samples for over 250 days after their preparation.

2. Experimental

The BSCCO samples were prepared using cationic ratio of Bi:Pb:Sr:Ca:Cu as 2.0: x :2.0:2.0:3.1 ($0.0 \leq x \leq 0.8$). In the first set of samples, called batch A, the powders were calcined at 800°C. The calcined mass was again heated at 800°C for 20 hr. In the second set of samples only two compositions, $\text{Bi}_2\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_{3.1}\text{O}_y$ (batch B) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3.1}\text{O}_y$ (batch C) were used. In this set too, the well-ground powders were pre-reacted at 800°C. The calcined mass was again ground and heated at 800°C for 2 hr followed by a slow increase in temperature to 820°C (\sim melting point of Bi_2O_3), which was maintained for 3 hr. Finally the temperature was raised to 840°C and maintained for 12 hr. The calcined mass so obtained was reground. The pellets, made at a pressure of 6 ton/cm², were first sintered in air at a temperature 3–4°C lower than their melting point for 20 min. They were then kept at a temperature 10°C lower than their melting point for different durations viz 75 to 125 hr. The pellets were cooled in O₂ till 500°C where they were kept for 24 hr before cooling to room temperature.

Rectangular bars (18 mm \times 2 mm \times 1 mm) were cut from sintered pellets for resistivity and J_c measurements. Resistivity was measured in the temperature range of 300–15 K by the d.c. four-probe method using indium contacts on silver electrodes. All J_c measurements were done at 77 K. J_c was calculated using the usual criteria of 1 $\mu\text{V}/\text{cm}$. For structural analysis X-ray diffraction data were obtained by employing Rigaku's RU 200 B X-ray diffractometer using CuK_α radiation.

3. Results and discussion

Figure 1 shows the variation of T_c with Pb concentration in the range $x = 0$ to 0.8 (samples A1 to A5). T_c maximizes at 105 K (sample A4) for $x = 0.6$. All the leaded samples showed single-step transition. The critical current density (figure 2) also showed similar variation as T_c and maximizes at 15 A/cm² for sample A4. Since $x = 0.6$ was the most appropriate Pb concentration from the point of view of both T_c and J_c , this concentration was selected for further investigations. The samples B1, B2 and B3

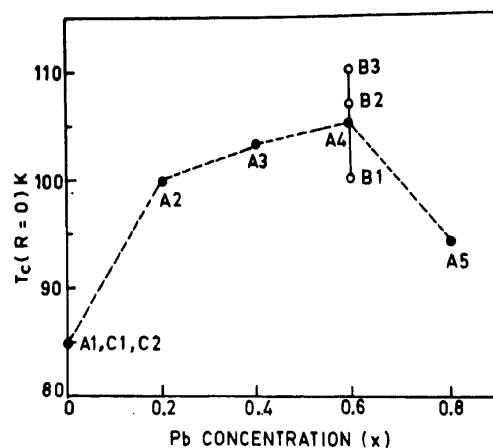


Figure 1. Variation of T_c with Pb concentration (samples A1 to A5) and sintering time (B1 to B3 and C1, C2).

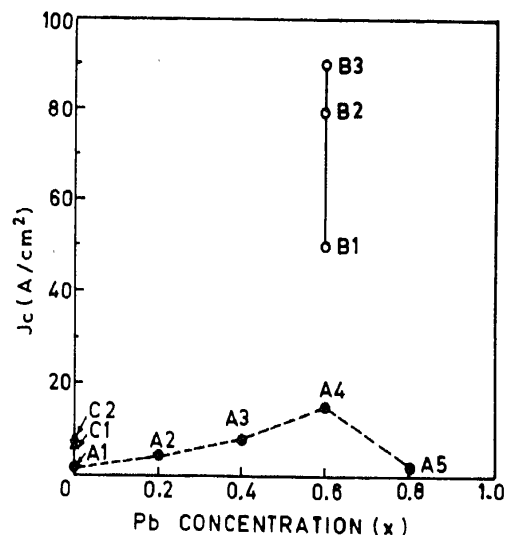


Figure 2. Variation of J_c with Pb concentration (samples A1 to A5) and sintering time (B1 to B3 and C1, C2).

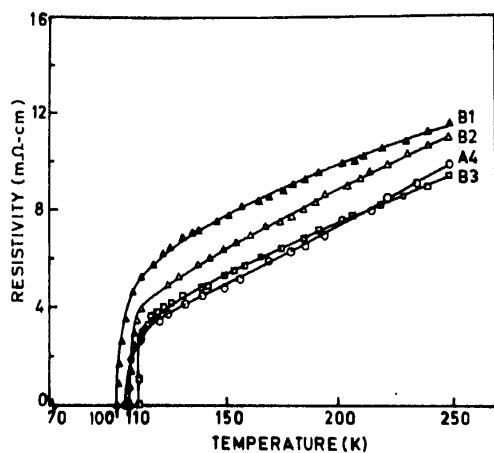


Figure 3. Temperature dependence of resistivity of samples B1, B2, B3 and A4.

were sintered for 75, 100 and 125 hr respectively. For comparison we include the results of lead-free samples, C1 and C2, sintered for 100 and 125 hr, respectively.

Whereas in lead-free samples (batch C) no improvement in T_c ($= 85$ K) was observed, the transition width and J_c improved over batch A. As shown in figure 2 J_c increased from 1 A/cm² (sample A1) to 6 A/cm² and 7 A/cm² for samples C1 and C2, respectively. In comparison, batch B samples showed an increase in both T_c and J_c . As shown in figure 3, all these samples exhibited a single-step transition with a T_c of 100, 107 and 110 K, respectively and the transition width narrowing down from 10 K for B1 to 2 K for B3. Associated with an improvement in T_c , an increase in J_c was also observed. The samples B1, B2 and B3 had a J_c of 50, 80 and 90 A/cm² (figure 2) respectively. It is thus

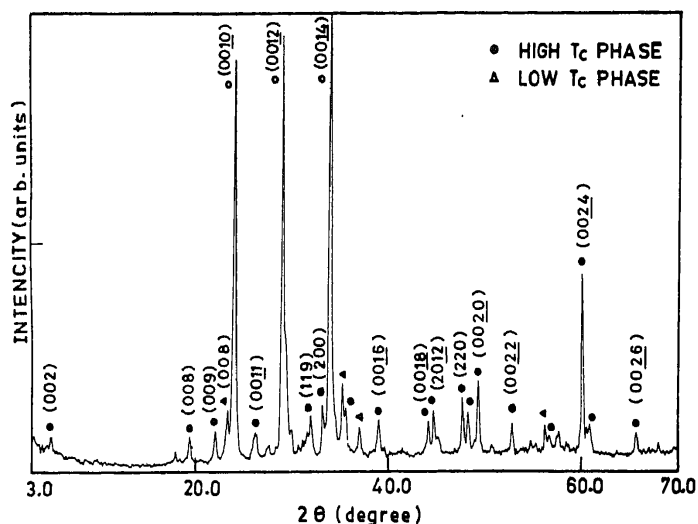


Figure 4. X-ray diffraction pattern of c -axis oriented sample B3. (●) High T_c phase, (▲) low T_c phase.

observed that the modification of the preparation condition leads to improvement in J_c by about an order of magnitude. This, in association with the Pb addition, improves J_c by two orders of magnitude.

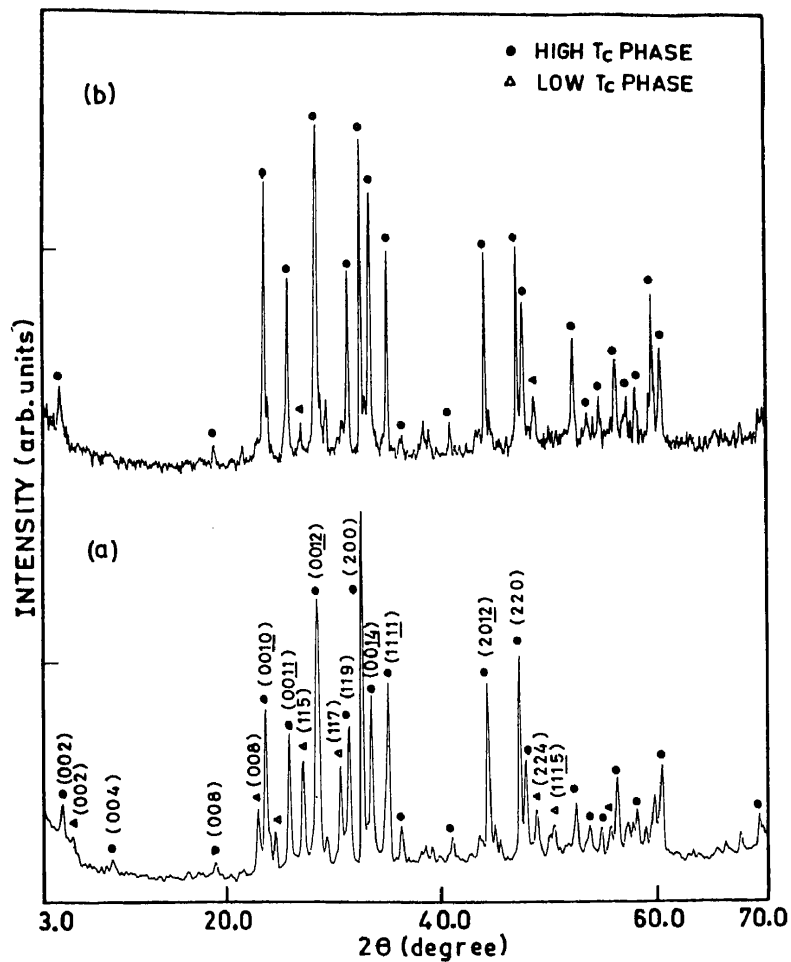
All the samples in batch A showed an orthorhombic structure (Gogia *et al* 1990) with coexistence of both—low and high T_c phases. However, no significant orientation effect was observed in these samples. In contrast, the samples in batch B showed strong orientation effects. The c -axis is oriented perpendicular to the sample surface as seen from figure 4 showing X-ray diffraction pattern of sample B3. With increase in sintering time, the extent of orientation increased and the low T_c phase content decreased. Lead-free samples (batch C) which exhibited predominantly low T_c phase also showed the same c -axis orientation effect. Therefore, the improvement in J_c in our batch B and C samples may be attributed to grain orientation (due to prereaction) and addition of lead (due to evolution of single 2223 phase).

It is clear from both electrical and structural properties of BSCCO superconductors that calcination at temperatures higher than the melting point of Bi_2O_3 after prereaction at 800°C helps in the formation of c -axis oriented nearly single high T_c phase thus improving J_c as well as T_c without requiring any special technique.

The environmental degradation behaviour of BSCCO superconductors was studied in terms of change in T_c , J_c and structure on exposure of these superconductors to atmosphere. The T_c and J_c of the two samples, one of lower T_c (A1) and the other of higher T_c (A4), were measured on 1st, 21st, 51st, 111th, 150th and 250th day of their preparation. X-ray patterns were also recorded on the same days. The T_c and J_c both decreased on exposure of samples to atmosphere. In case of A1, T_c continuously decreased from 85 to 65 K till 250 days after its preparation. In leaded superconductor (sample A4), T_c had gone down from 105 to 98 K at the end of 111 days after which it became almost constant at 97 K till 250 days. This suggests a remarkable improvement in atmospheric stability of leaded BSCCO superconductor. Changes in J_c were also minimal for A4. The values of T_c and J_c are presented in table 1.

Table 1. Variation of T_c and J_c of samples A1 and A4 with exposure time to atmosphere.

Day	A1 ($x=0.0$)		A4 ($x=0.6$)	
	T_c (K)	J_c (A/cm ²)	T_c (K)	J_c (A/cm ²)
1	85	1.0	105	15
21	80	0.4	103	14
51	76	—	101	13
111	71	—	98	12
150	68	—	97.5	11
250	65	—	97	10

**Figure 5.** X-ray diffraction patterns of sample A4 recorded on (a) 1st day of its preparation and (b) after 250 days of preparation.

Structural analysis of A4 showed some striking features. This sample initially had both low and high T_c phases (figure 5a) which were clearly discernible. But after 50 days a predominantly high T_c phase was observed with almost sudden decrease in intensities of low T_c phase peaks. Beyond this period no further change (figure 5b) was observed. It looked as if lead had completely stabilized the high T_c phase. In sharp contrast to A4, sample A1, which initially had a few low intensity peaks of high T_c phase along with dominant peaks corresponding to low T_c phase, showed almost complete disappearance of high T_c phase on exposure of these samples to atmosphere. This conforms with the vanishing of the step in resistivity measurements corresponding to the high T_c phase. It is clear that low T_c phase is quite stable in the Pb-free sample but not the high T_c phase. However, once the high T_c phase is stabilized with the addition of Pb, it does not degrade structurally on exposure to atmosphere. It is suggested that the observed decrease in T_c and j_c of leaded BSCCO superconductor when exposed to atmosphere is not a bulk degradation phenomenon but may be due to surface degradation as a result of carbonate/hydroxide formation on the surface.

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