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Further studies on Ag/BPSCCO tapes using low purity materials

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Abstract. Transmission electron microscopic (TEM) studies are reported on Ag-clad $Bi_{1\cdot7}Pb_{0\cdot4}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ tapes prepared by using low purity (98–99%) commercial grade materials. The self-field J_c values of these tapes viz. $6\cdot14 \times 10^3$ A.cm^{-2} at 77 K and $1\cdot4 \times 10^5$ A.cm^{-2} at 4·2 K, reported in an earlier publication, were significantly higher than the corresponding J_c values in tapes prepared with high purity (99·99%) materials. The TEM pictures on the low purity core material of the tapes reveal the presence of stacking faults and the intergrowth of the 2212 and 2223 phases which could be acting as flux pinning sites and responsible for enhanced J_c values. These defects can perhaps be traced back to the presence of 60 ppm iron in the low purity CuO as revealed by atomic absorption analysis reported earlier.

Keywords. Critical current density; Ag-clad BPSCCO tapes; structural inhomogeneities.

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In an earlier paper, Shukla *et al* [1] reported a marked improvement in the critical current density (J_c) of Ag-clad $Bi_{1\cdot7}Pb_{0\cdot4}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ (BPSCCO) tapes when constituent oxides and carbonates of low purity (98–99%) were used. The highest J_c values obtained in these studies were $6\cdot14 \times 10^3$ A.cm^{-2} (77 K, 0T) and $1\cdot4 \times 10^5$ A.cm^{-2} (4·2 K, 0T). These values were significantly higher than those obtained in Ag-clad Bi (2223) tapes prepared using high purity (99·99%) materials [2] and processed in an almost identical manner. The motivation behind these studies [1] was two fold. Firstly, the use of low purity commercial grade material's being economical is important from the production point of view. Secondly, the small amount of impurities present in the low purity constituent oxides/carbonates could cause structural inhomogeneities which could act as flux pinning sites and enhance J_c values. It was also reported by us that CuO used in these studies contained 60 ppm iron as revealed by atomic absorption studies. It was conjuctured that this iron could be responsible for higher values of J_c through enhanced flux pinning.

In this brief communication we report our TEM studies carried out on some of these tape specimens. The studies showed some structural features which could be traced back to the presence of this small amount of iron impurity and a minor (2212) phase in an otherwise major 2223 phase.

The details of the tape fabrication have been described elsewere [1]. The core material with a composition $Bi_{1\cdot7}Pb_{0\cdot4}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ was prepared by the usual solid state diffusion method. The starting materials were Bi_2O_3 (99%), PbO (98%), $Sr(NO_3)_2$ (99%), $CaCO_3$ (99%) and CuO (99%), all of commercial grade purity. The

Table 1. Ag-clad $Bi_{1\cdot7}Pb_{0\cdot4}Sr_{1\cdot8}Ca_2Cu_{3\cdot5}O_x$ tape specimens with low purity starting materials.

Set no.	Specimen no.	Core size t(mm) × w(mm)	J_c(77 K) A.cm^{-2}	J_c(4.2 K) A.cm^{-2}
One	40	0·22 × 0·68	220	7700
	41	0·14 × 0·71	320	11000
	42	0·009 × 0·89	3750	131000
Two	45	0·18 × 0·71	580	8200
	46	0·08 × 0·80	1020	18300
	48	0·007 × 0·93	6140	149000

tapes were prepared by the usual powder-in-tube technique. Tapes of different thicknesses between 0·74 mm and 0·24 mm were prepared and sintered at 845°C for 20 h in air. These specimens are referred to as specimen nos 40, 41 and 42 shown as set no. 1 in table 1. Parts of these tapes were rolled again and sintered at 845°C for 20 h. These specimens are designated as specimens 45, 46 and 48 respectively and shown as set no. 2 in table 1. The specimen 48 is 0·14 mm thick with a core thickness of 7 μm. The grain structure as revealed by SEM has already been reported [1]. Successive rolling leads to an improved grain structure. The XRD spectra showed the presence of a predominantly 2223 phase with a 2212 phase as a minor fraction. The 2223 phase fraction increases with repeated rolling and sintering and the (001) reflections become sharp indicating grain alignment (c-axis texturing). Detailed microstructural analysis was carried out on a few specimens using a TEM model JCM 200 cx operating at 160–200 kV. The J_c of all the tape specimens was measured at 77 K and 4·2 K using a four-probe method and following a criterion of 1 μV/cm.

Table 1 gives the composition, sintering parameters, dimensions of the cores and the measured J_c values. These J_c values at 77 K and 4·2 K are plotted as a function of inverse of core thickness (t^{-1}) in figure 1. For comparison similar plots (J_c vs t^{-1}) for tape specimens with high purity (99·99%) starting materials which were earlier reported [2] are also shown in figure 1. As seen in the figure J_c increases with repeated rolling and sintering in conformity with earlier reports in the Bi-2223 system [2, 3, 4]. At 4·2 K J_c values of the tapes of set nos 1 and 2 lie on a single curve as both the phases of the Bi-system (2212 and 2223) are known [5] to carry identical currents at 4·2 K. J_c varies as t^{-1} similar to that reported earlier by Osamura *et al* [6] and Dersch and Blatter [7].

As mentioned earlier. 99% pure CuO was used while preparing the core material for the tapes. The atomic absorption spectroscopic analysis of CuO shows the presence of 60 ppm iron in it. To understand the role of iron in influencing the superconducting properties, it is important to know which site iron occupies in the Bi-system, superconducting properties being extremely sensitive to the Cu-sites. Mössbauer studies by Tang *et al* [8] carried out on a variety of BSCCO superconductors with the addition of 1·5% Fe in place of copper, show that iron substitutes the Cu (II) sites (square pyramidal) in the 2223 phase. This results in stacking faults and the intergrowth of different phases. These defects can enhance flux pinnings. Large intragranular pinning forces have indeed been reported by Wordenweber *et al* [9] in $YBa_2(Cu_{1-x}Fe_x)_3O_y$ (for $x \leqslant 0{\cdot}01$) which is isostructural to the BSCCO system. TEM micrograph on the core material of the tape specimen no. 48 indeed shows a typical lattice fringe

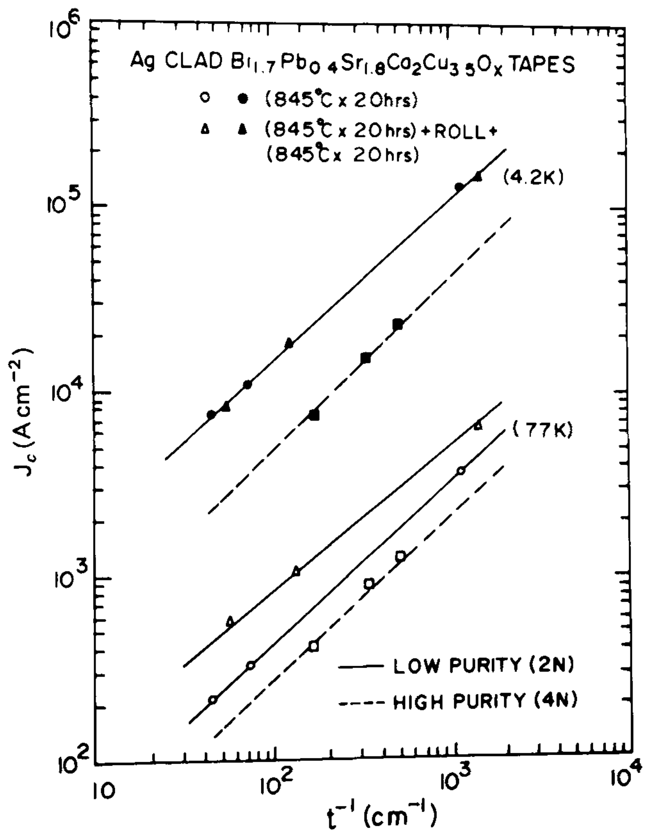

Figure 1. J_c at 77 K and 4·2 K of the tape specimens listed in table 1 plotted against inverse of core thickness (t^{-1}). For comparison J_c vs t^{-1} plots of the tape specimens prepared with high purity materials [2] are also included (dotted curves).

image displaying high density of stacking faults (figure 2). The micrograph reveals slight bending of the lattice fringes. The lattice spacing changes from one region to another. The lattice expansion occurring in one region causes a bent in the lattice, as seen in the TEM micrograph. The inset in figure 2 is the corresponding selected area electron diffraction pattern (SAEDP) showing an incommensurate structure.

In intergrowth of the two phases viz., 2212 and 2223 with two fringe spacing of 30·0 Å and 36·7 Å corresponding to the c-axis parameters of the two phases respectively are seen in the same specimen (figure 3). This is in conformity with the XRD studies which show the presence of the two phases (2223 and 2212) in the ratio 60:40 in the bulk material as determined by the relative intensities of the (002) reflections. Although the volume fraction of 2223 phases increases in the tapes of the second set yet the 2212 phase is still present (8% in specimen no. 48). The presence of the 2212 phase dispersed in the 2223 phase matrix must have beneficial effect on flux pinning. It has indeed been suggested [10] that the 2212 phase may act as potential flux pinning centres in these materials leading to high J_c values. The presence of the 2212 phase is however common to the tapes of the present studies as well as the tapes using high purity materials of the previous studies [2]. The significantly high values of J_c in low purity tapes can then be attributed to the stacking faults caused by the substitution of iron, present as an impurity in CuO, at the copper site. Systematic studies with

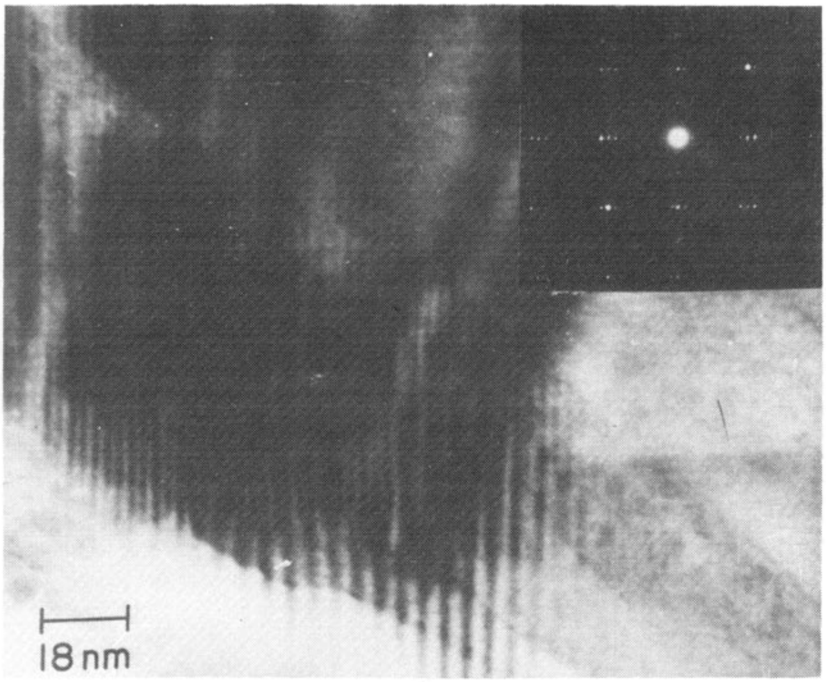

Figure 2. Lattice fringes image of tape specimen no. 48 showing high density of stacking faults. The picture shows slight bending of the lattice fringes and consequently the lattice spacing changes in different regions. The corresponding SAEDP reveal an incommensurate structure as seen in the inset.

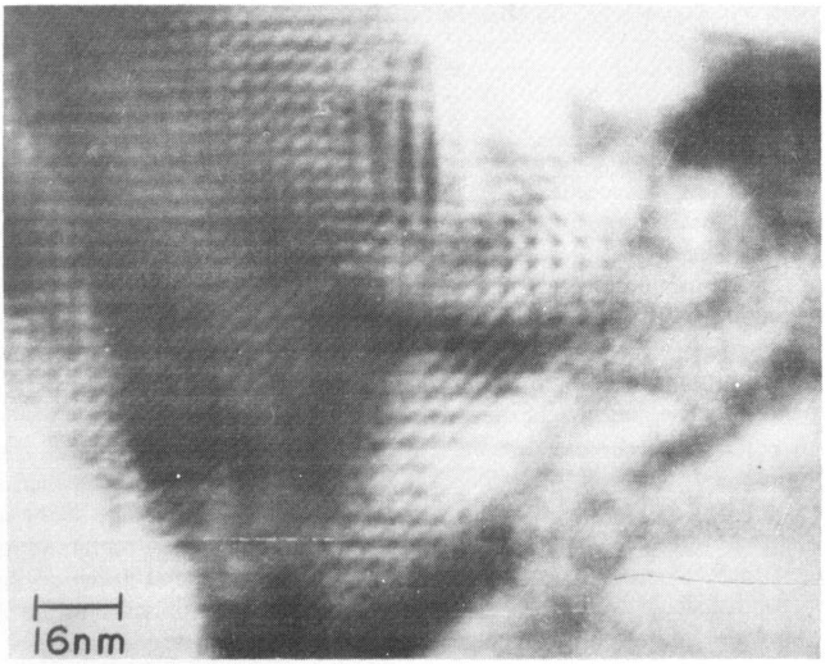

Figure 3. TEM micrograph of specimen no. 48 showing the intergrowth of two phases viz., low T_c (2212) and high T_c (2223) with a c-axis parameter equals to 30 Å and 36·7 Å respectively.

the addition of varying amounts of Fe in the B(P)SCCO materials are, however essential to confirm these conclusions. Such experiments are in progress.

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References

[1] S R Shukla, Y S Reddy and R G Sharma, *Pramana–J. Phys*, **38**, 179 (1992)
[2] S R Shukla, Y S Reddy D K Pandya, Y Tanaka and R G Sharma, *Pramana–J. Phys.* **37**, 333 (1991)
[3] T Asano, Y Tanaka, M Fukotomi, K Jikihara and M Maeda, *Jpn. J. Appl. Phys.* **28**, L595 (1988)
[4] K Togano, H Kumakura, H Maeda, E Yanagisiwa, N Irisawa, J Shimoyama and T Morimoto, *Jpn. J. Appl. Phys.* **28**, L95 (1989)
[5] H Kumakura, K Togano, H Maeda and M Mimura *J. Appl. Phys.* **67**, 3443 (1990)
[6] K Osamura, T Tokayama and S Ochiai, *Cryogenics* **29**, 430 (1990)
[7] H Dersch and G Blatter, *Phys. Rev.* **B38**, 11391 (1988)
[8] H Tang, Z Q Qiu, Y W Du and J C Walker, *J. Appl. Phys.* **67**, 4512 (1990)
[9] R Wordenweber, G V S Sastry, K Heinemann and H C Freyhardt, *J. Appl. Phys.* **65**, 1648 (1989)
[10] S X Dou, Y C Gou and H K Liu, *Physica* **C194**, 343 (1992)