

# Improvement of Critical Current Density in Thallium-Based (Tl,Bi)Sr<sub>1.6</sub>Ba<sub>0.4</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Superconductors

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## Abstract

Epitaxial (Tl,Bi)Sr<sub>1.6</sub>Ba<sub>0.4</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> ((Tl,Bi)-1223) thin films on (100) single crystal LaAlO<sub>3</sub> substrates were synthesized by a two-step procedure. Phase development, microstructure, and relationships between film and substrate were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Resistance versus temperature, zero-field-cooled and field-cooled magnetization, and transport critical current density ( $J_c$ ) were measured. The zero-resistance temperature was 105–111 K.  $J_c$  at 77 K and zero field was  $> 2 \times 10^6$  A/cm<sup>2</sup>. The films exhibited good flux pinning properties.

## Introduction

An important step in understanding of flux pinning in high- $T_c$  superconductors was the prediction by Kim et al. that flux pinning should improve as the layers between Cu-O planes become thinner [1]. The model of Kim et al. stimulated interest in Tl-based 1212 and 1223 superconductors because of their thin insulating layers relative to Tl-2212, Tl-2223, Bi-2212, and Bi-2223 types. Tl-1212 and Tl-1223 tapes with  $J_c$  to  $2 \times 10^4$  A/cm<sup>2</sup> at 77 K and zero field have been fabricated by the powder-in-tube method [2-18]. However, attempts at further improvement have met with little success, in spite of the worldwide effort, due mainly to weak-link problems. The transport  $J_c$  of these tape samples often decreased by a factor of 20 at 77 K as the external magnetic field was raised from 0 to 0.2 T [10].

The intrinsic flux pinning properties of the bulk samples was quite good: for example,  $J_c$  decreased only by a factor of 3 at 77 K as the field was increased from 0.2 to 5.5 T. The best bulk samples are probably the thick films reported by General Electric [19-21], and Tl-1223 tapes electrodeposited on metallic silver and annealed in a two-zone furnace [22]; however, weak links continue to be a serious problem in these samples. Thin films are well known to have high transport  $J_c$  and excellent flux pinning at 77 K. We have, therefore, directed our efforts toward the fabrication of Tl-based 1223 thin films. We have successfully made epitaxial (Tl, Bi) $Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$  ((Tl,Bi)-1223) thin films with high  $J_c$  in magnetic field for the first time [23]. In this paper, we report on microstructural development and superconductivity as functions of temperature and heat treatment.

## Experimental Details

The films were prepared by laser ablation. A pellet of composition  $Tl_{0.95}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$  was prepared by pressing an intimate mixture of 0.475  $Tl_2O_3$  + 0.11  $Bi_2O_3$  +  $Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$  in a 1.28 cm die at a pressure of 150 MPa. The pellet was placed between gold plates, wrapped in silver foil, sintered in air at 870–900°C for 3–5 h, cooled, and then pulverized. The source pellet for film fabrication was made by mixing 1 FW of the above powder with 0.475 FW  $Tl_2O_3$  and 0.4 FW CaO, and pressing at 750 MPa in the 1.28 cm die. Laser ablation was conducted at 120 mJ/pulse, 21 KV, and 2–10 pulse/s; substrate temperature was 300–500°C. Films were deposited on (100) single-crystalline  $LaAlO_3$ . The resulting films were placed between  $Tl_{0.95}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$  pellets and set on a gold plate. This assembly was wrapped in silver foil with a plenum space, and heated in air at 840–870°C for 25–60 min.

The phase structure and mosaic distribution of the films were measured by  $2\theta$  scans and rocking curves. The relationship between the film and substrate was determined by both X-ray  $\phi$  scans and TEM. Microstructures were characterized by SEM, energy dispersive spectroscopy (EDS), and TEM. Magnetization versus temperature was measured by DC SQUID. DC zero-resistance temperature ( $T_c$ ) and transport  $J_c$  were measured by standard four-probe methods. Films were 1  $\mu m$  thick and were patterned into 90 x 200  $\mu m$  microbridges by photolithography. Four silver contacts were deposited onto each film. Measurements of  $J_c(H)$  were performed in a DC SQUID, with the magnetic field aligned perpendicular to film c-axes.

## Results and Discussion

**1. Phase development:** Figure 1a shows the morphology of the precursor films; Figs. 1b and 1c show the annealed films. The precursor films consisted of uniform small particles. Although the ablation source was Tl-rich ( $Tl_{1.8}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$ ), the content of Tl in the precursor was substoichiometric (Table 1). There were many more acicular grains in Fig. 1b than in Fig. 1c. These grains were found to have a-axis orientation. The

Table 1. Average composition of precursor and annealed films.

	Tl	Bi	Sr	Ba	Ca	Cu
Precursor	0.7	0.2	1.6	0.3	2.7	2.5
Annealed film 1	0.7	0.2	1.6	0.4	2.3	2.8
Annealed film 2	0.7	0.2	1.6	0.2	2.8	2.5

average composition, determined by EDS, of the annealed films with fewer acicular grains was 0.9/1.9/2.3/2.9, which was close to stoichiometric 1223. The films with more acicular grains had an average composition of 0.9/1/8/2.8/2.5, further from the ideal stoichiometry.

Annealing temperature was a key parameter for 1223 phase development. At low temperature (820°C), we obtained only 1212 phase. As the temperature increased, the 1223 phase gradually formed (Fig. 2). At 840°C, the sample consisted of 1223 and 1212 phases. Although the 1223 phase was dominant, the XRD peaks of 1212 phase were still strong (shown by the relative intensity of the (004) peak of 1212 vs. that of the (005) peak of the 1223, and of the (005) peak of the 1212 to the (006) peak of the 1223). At 860°C, the peaks of 1212 phase were barely distinguishable.

Another key parameter for 1223 phase development was annealing duration. Samples were heated at 860°C for different lengths of time. For short time at temperature, 1212 formed (Fig. 3). For longer annealing times, more and more 1223 phase formed. After 60 min, the 1212 phase completely transformed into 1223. Rocking curves of the (006) peak of the 1223 were examined for several films. The typical full width at half maximum (FWHM) was 0.365°, which is comparable with high-quality YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> films. We concluded that the optimal annealing temperature and time were 860°C and 60 min, respectively.

**2. Microstructure and Orientation:** From the XRD patterns, it was clear that the films were highly phase pure and c-axis oriented. We investigated the epitaxy between film and substrate by both X-ray  $\phi$  scans and TEM. To determine the in-plane orientation between the (Tl,Bi)-1223 film and LaAlO<sub>3</sub> substrate, we measured  $\phi$  scans of the (103) film reflection and the (222) substrate reflection (Fig. 4). The [100] axis of (Tl, Bi)-1223 overlapped with the [100] of LaAlO<sub>3</sub>. This epitaxial growth is reasonable because the lattice mismatch between [100] of (Tl, Bi)-1223 and [100] of LaAlO is only 0.5%.

Figure 5a shows a typical area of the epitaxial film and a misoriented grain. This misoriented grain could be either intrinsic or caused by sample preparation. Figure 5b shows dislocations within the film near the interface.

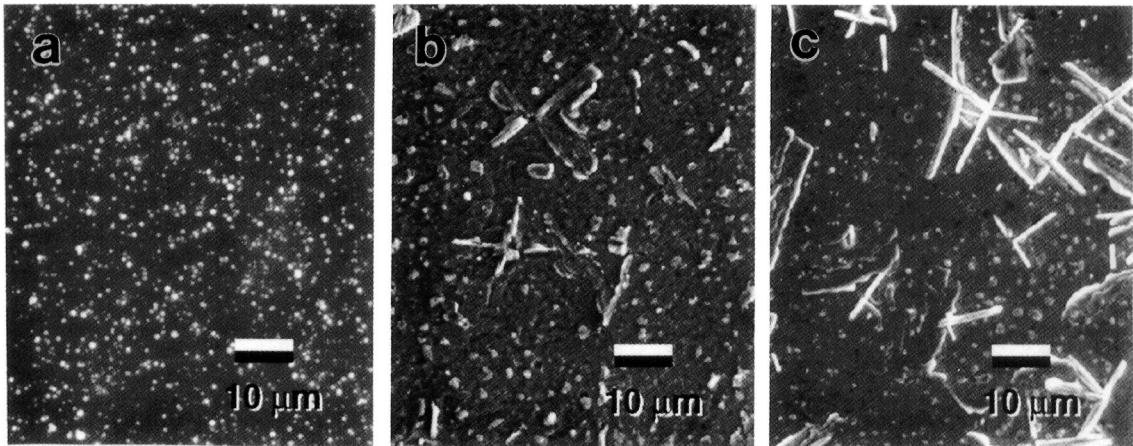


Fig. 1. SEM photomicrographs of precursor and annealed films.

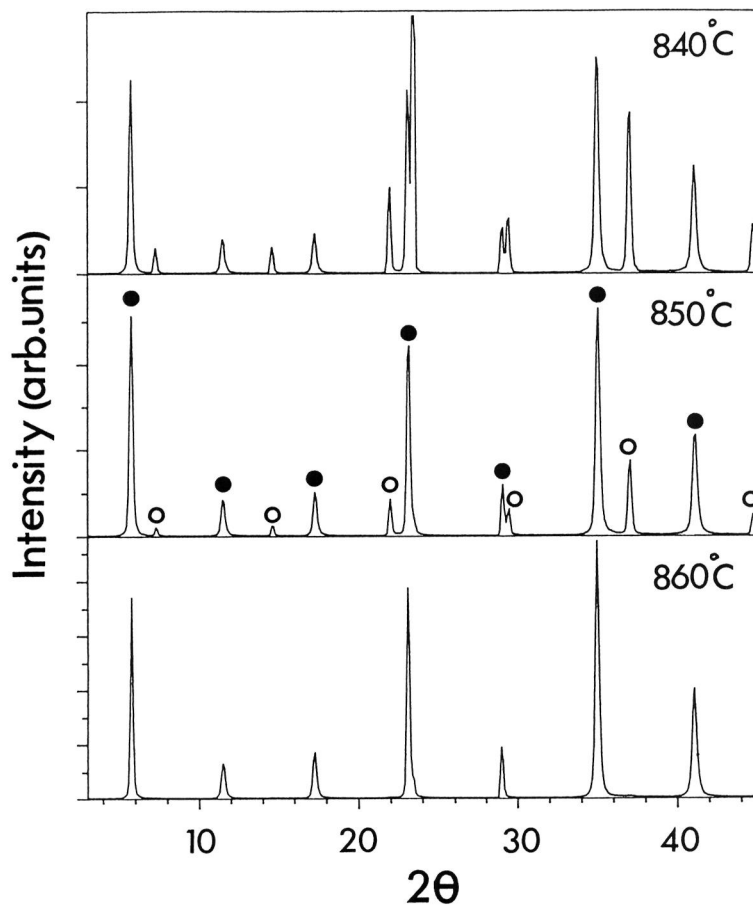


Fig. 2. XRD plots of films annealed as shown; only  $(00l)$  peaks are present;  $(\text{Tl,Bi})\text{-1223}$  marked by filled circle,  $(\text{Tl,Bi})\text{-1212}$  by open circle.

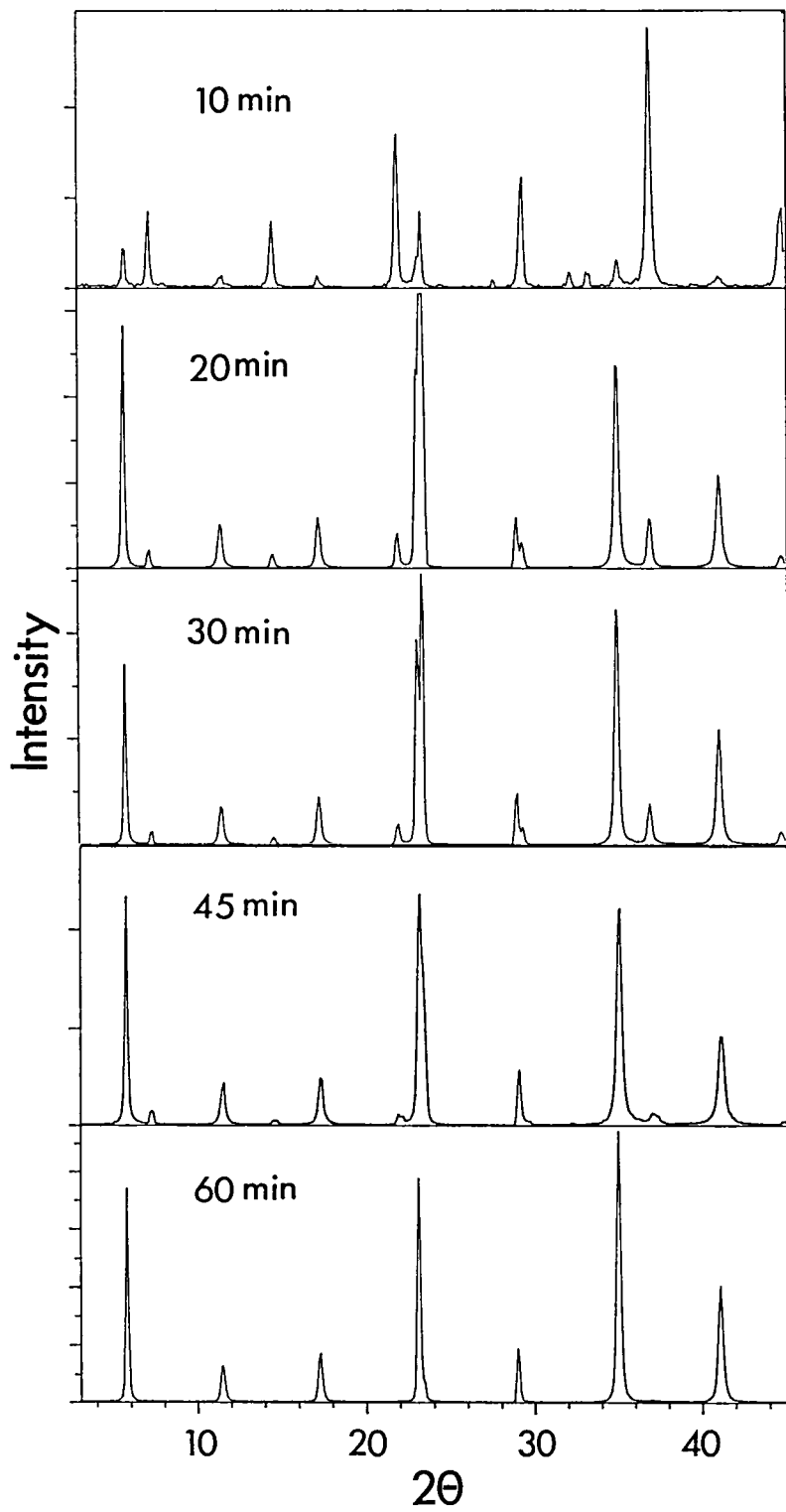


Fig. 3. XRD plots of (Tl,Bi)-1223 films annealed at 860°C in air.

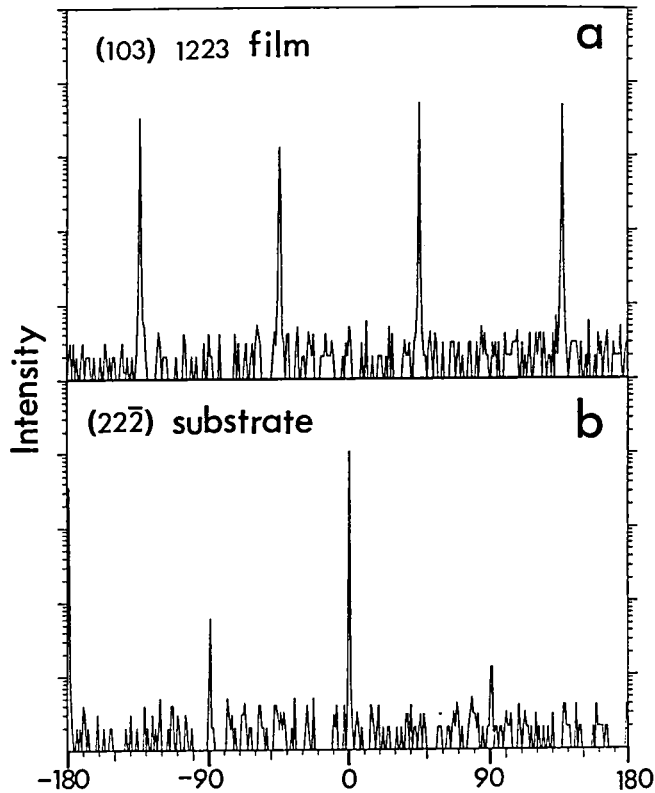


Fig. 4. XRD  $\phi$  scans of (a) (Tl,Bi)-1223 film and (b)  $\text{LaAlO}_3$  substrate.

Figure 6a is a high-resolution image of the interface. A semi-periodic contrast and a few small defects were observed. The contrast was due to strain caused by the lattice mismatch between the film single-crystal substrate. Figure 6b shows a thin layer near the interface containing dislocations and a region above the layer containing many stacking faults. There was a slight rotation between the two areas, as confirmed by convergent-beam electron diffraction.

**3. Superconductivity:** Figure 7 shows two typical  $T_c$  curves.  $T_c$  was 105–111 K, and depended on phase purity. For many measurements, we found that samples with pure Tl-1223 phase had  $T_c$  of 105–107 K (Fig. 7a), whereas films with a little 1212 phase had a higher  $T_c$  of  $\approx$  111 K (Fig. 7b). This phenomenon has yet to be clearly understood.

Figure 8 shows typical zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves measured at 20 G with the field parallel to the c-axis of the (Tl,Bi)-1223 film. The transition onset was 105 K, which was lower than the DC zero resistance of 107 K. If we assume flux exclusion was 100% at the lowest measured temperature of the ZFC curve, the flux expulsion measured by FC would be  $\approx$  3%, which would reflect highly incomplete flux expulsion. Incomplete flux expulsion could originate for several possible reasons: flux pinning, the Ebner-Stroud superconduction glass model, or less than full superconductivity of sample [24]. The last two causes require presence of

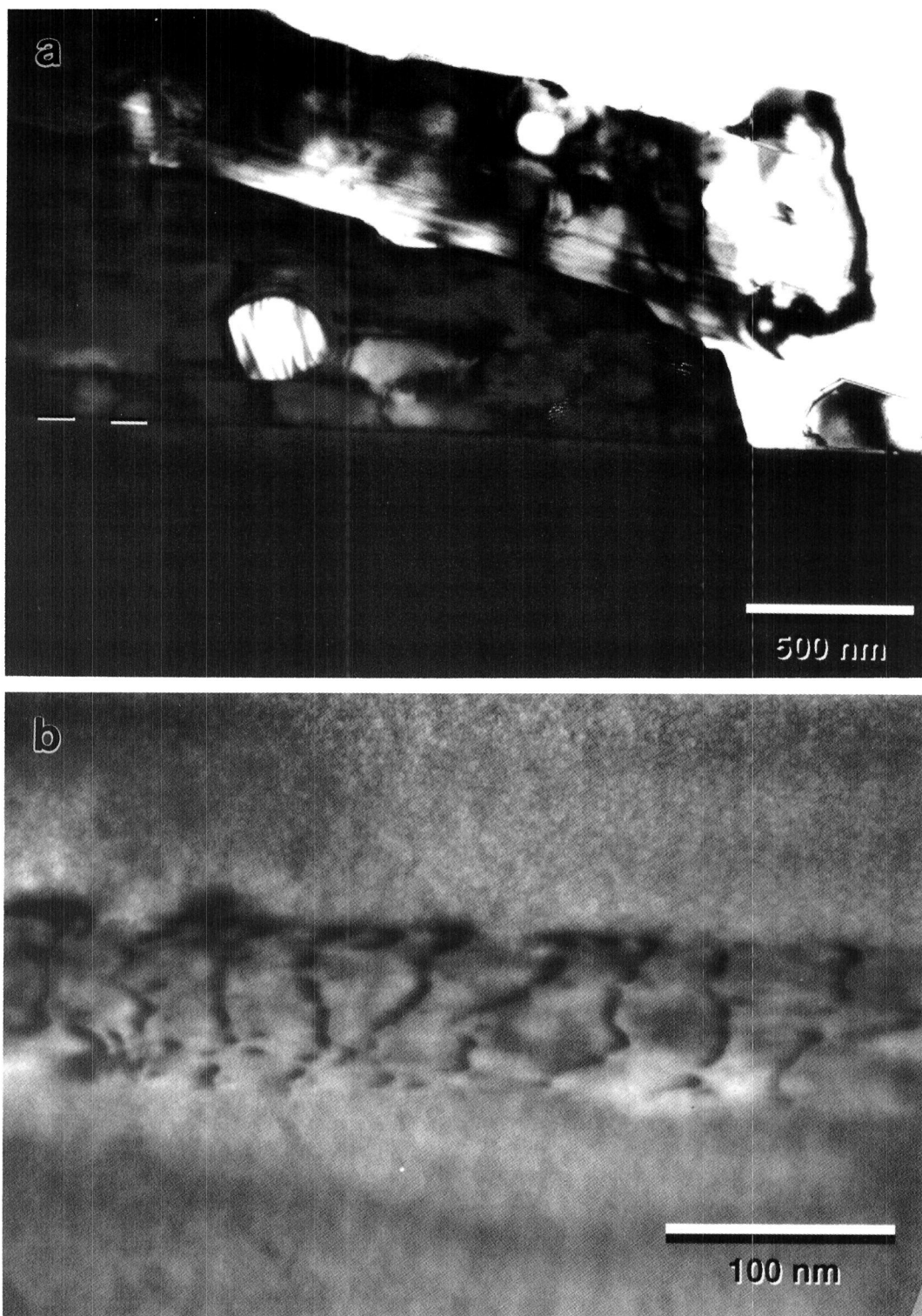


Fig. 5. TEM photomicrograph of (a) typical area of epitaxially grown (Tl,Bi)-1223 film and (b) dislocations in film at  $\text{LaAlO}_3$  interface.

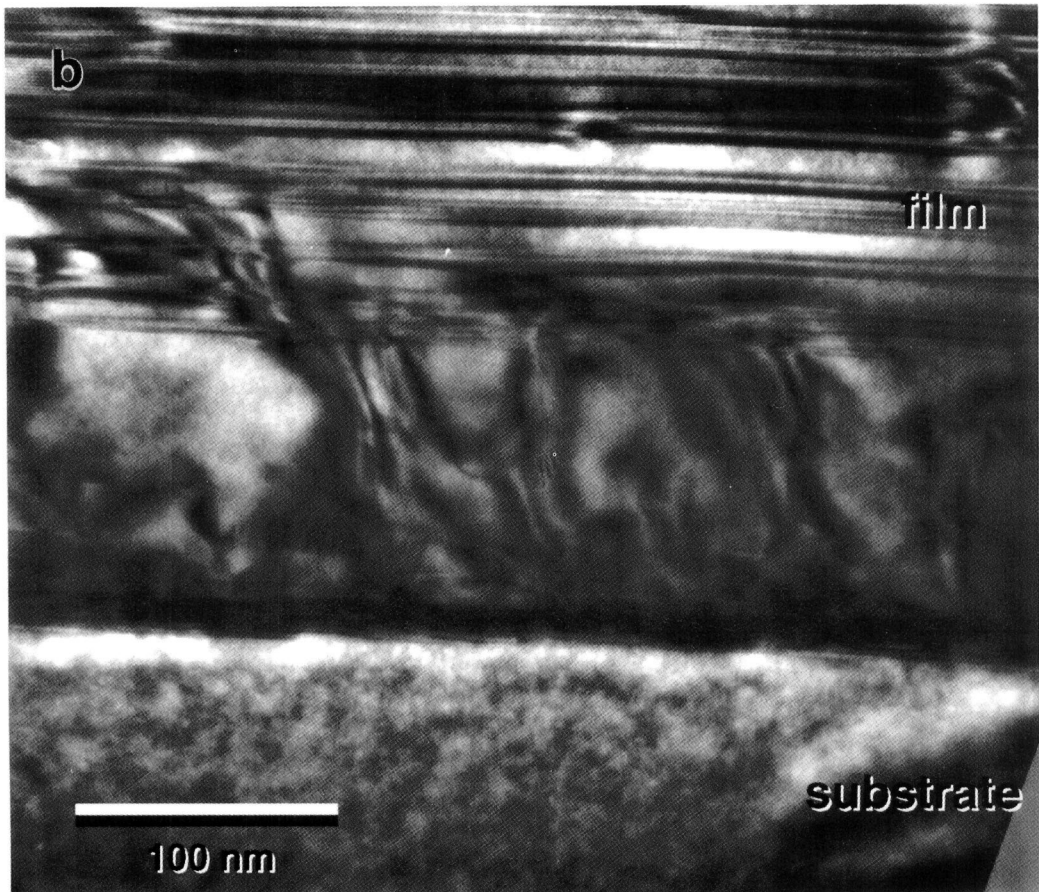
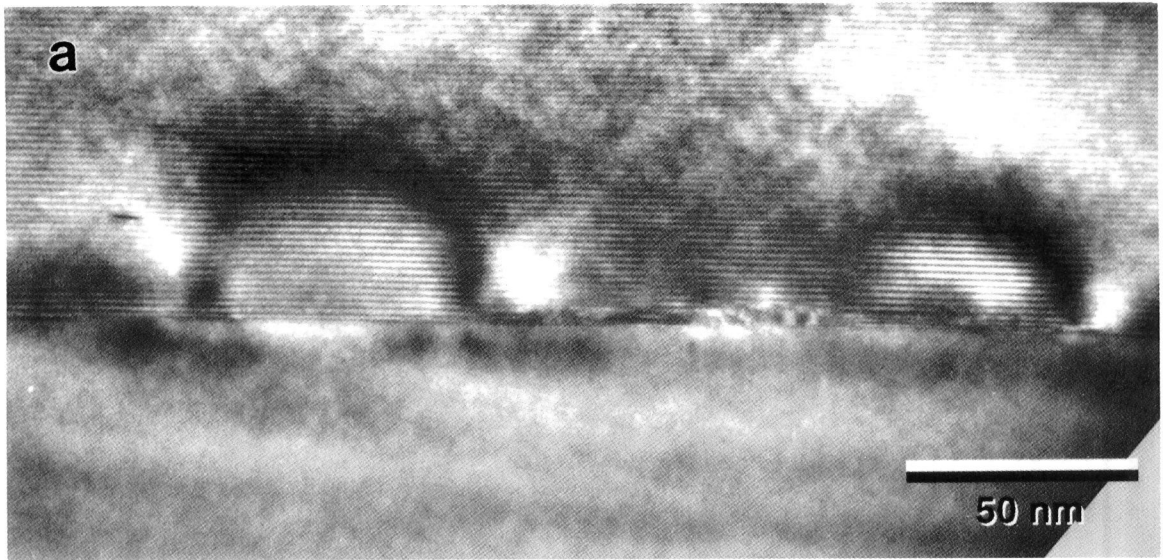


Fig. 6. High-resolution TEM photomicrographs of (a) semi-periodic lattice strain caused by lattice mismatch between (Tl,Bi)-1223 film and  $\text{LaAlO}_3$  interface and (b) dislocations near interface.



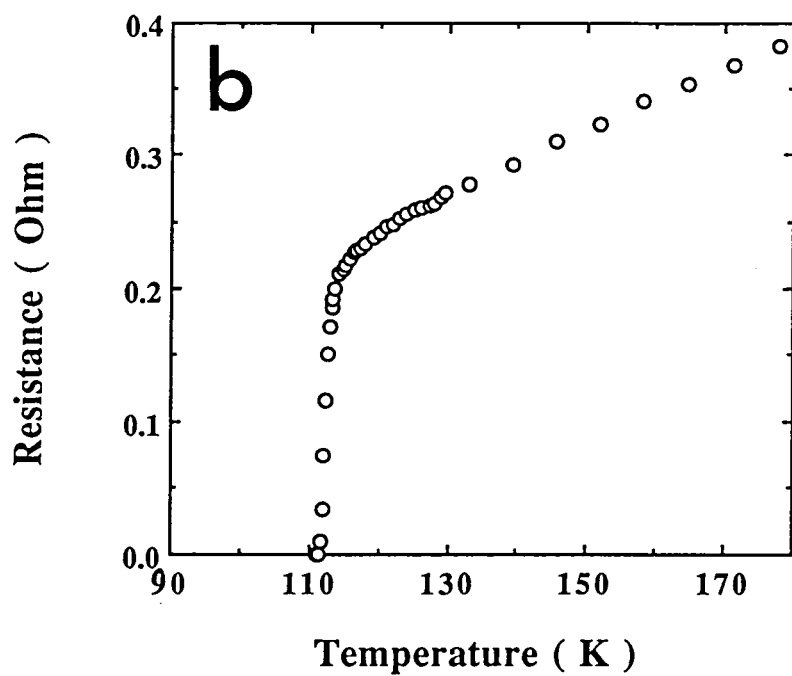
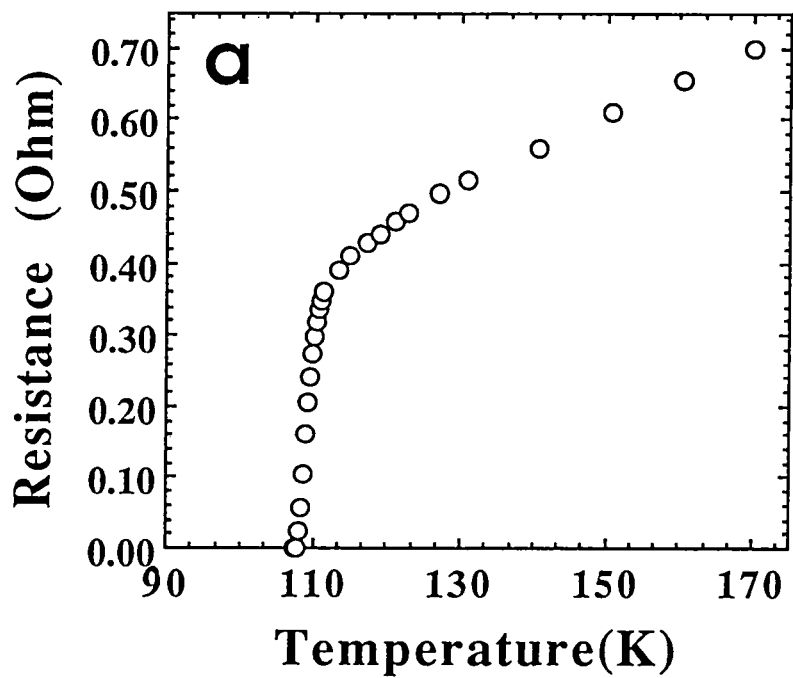


Fig. 7. Typical resistance vs. temperature curves for (a) films with a little (Tl,Bi)-1212 and (b) pure (Tl,Bi)-1223 films.

weak links. The transport  $J_c$  data discussed below indicate the absence of significant weak links in our films and suggest that the observed incomplete flux expulsion is due to strong flux pinning.

Defects such as twin boundaries [25] and a-axis oriented plates [26] have been observed to be effective pinning centers, in addition to the intrinsic pinning between Cu-O layers [27]. Several defects in our films that may perhaps be partly responsible for good flux pinning were observed by TEM.

The results of  $J_c(H)$  measurements are shown in Fig. 9. The insert shows the clear  $J_c$ - $H$  relationship at low magnetic field. At 67 K,  $J_c$  did not decrease from 0 to 0.1 T, and, surprisingly, there was a small increase below 200 G. At 87 K, an obvious increase was observed, and then  $J_c$  decreased for  $H > 0.1$  T. At 77 K and 5.5 T,  $J_c$  was  $5 \times 10^5$  A/cm<sup>2</sup>. At 87 K and 5.5 T,  $J_c$  remained  $> 10^5$  A/cm<sup>2</sup>. Because of the limited chamber size in the SQUID, to date we have managed to measure  $J_c$  with  $H$  perpendicular to c-axis only. The  $J_c$ - $H$  dependence for  $H$  parallel to c-axis is now being studied.

## Conclusions

(Tl,Bi)Sr<sub>1.6</sub>Ba<sub>0.4</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> films were epitaxially grown on (100) LaAlO<sub>3</sub> single crystals. Both c-axis and a-b-axis alignment were achieved.  $T_c$  was 105–111 K and depended on phase purity. Samples with some 1212 phase had  $T_c$  of  $\approx 111$ K; phase-pure samples had  $T_c$  of  $\approx 105$ –107 K.  $J_c$  at 77 K and zero field reached  $2 \times 10^6$  A/cm<sup>2</sup> when measured on a 1  $\mu$ m thick, 90  $\mu$ m wide, 200  $\mu$ m long microbridge.  $J_c$  was  $5 \times 10^5$  A/cm<sup>2</sup> with a 5.5 T magnetic field applied perpendicular to the c-axis.

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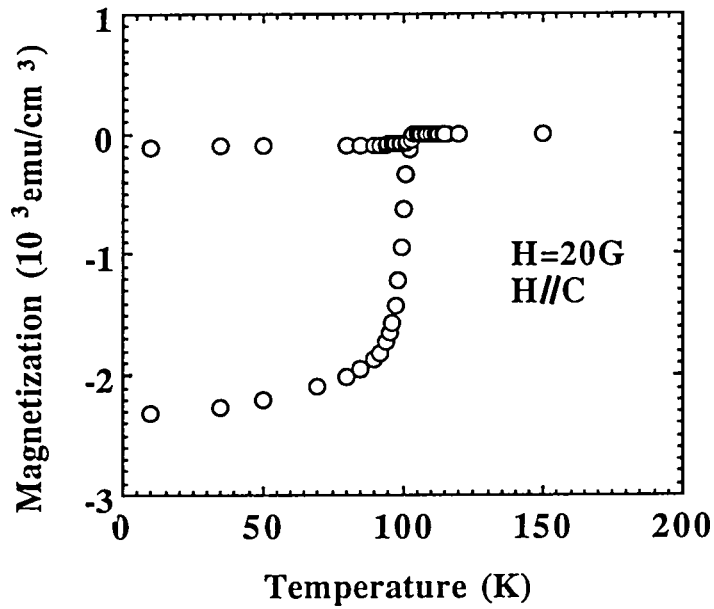


Fig. 8. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization of (Tl,Bi)-1223 film measured in field of 20 G.

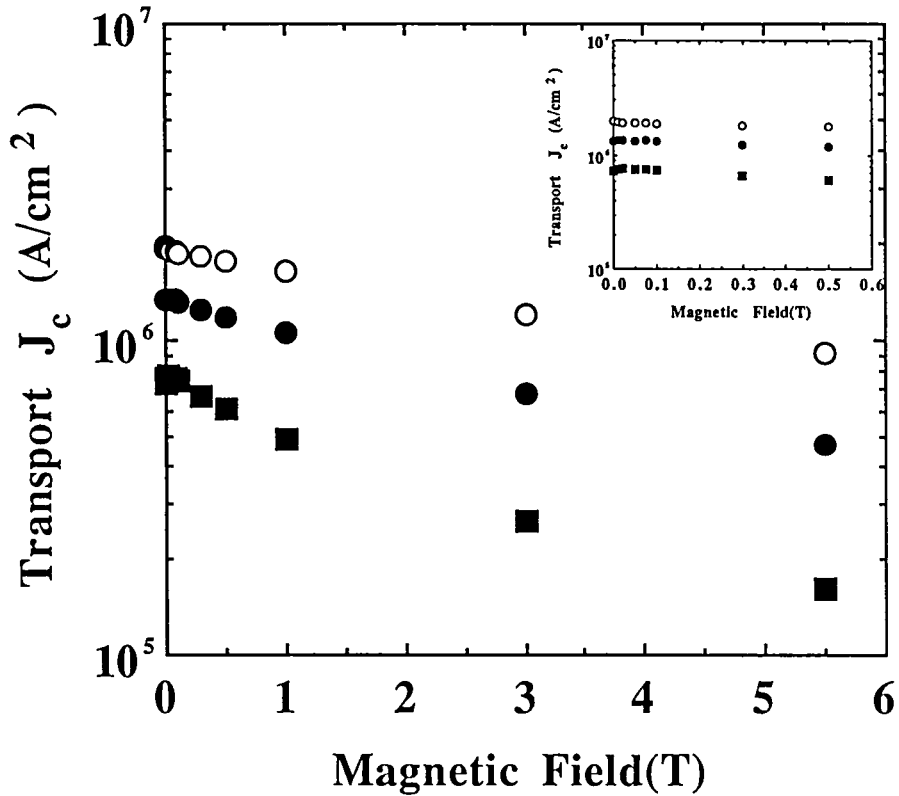


Fig. 9. Relationship between transport  $J_c$  and field with H perpendicular to c axis: 67 K (open circles, 77 K (filled circles, and 87 K (filled square).

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