

Evidence for local composition variations within $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries

S. E. Babcock and D. C. Larbalestier

Applied Superconductivity Center & Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706

(Received 7 April 1989; accepted for publication 26 May 1989)

The composition variations associated with grain boundaries in bulk sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been investigated by means of energy-dispersive x-ray microanalysis in a high spatial resolution scanning transmission electron microscope. A series of composition profiles indicates that considerable variations in composition occur on a very local scale both parallel and perpendicular to these grain boundaries. The regular, oscillatory (period ~ 25 nm) nature of the composition variations observed along a grain boundary suggests that these heterogeneities may be an intrinsic feature of the boundary. Some possible implications of these observations for percolative conduction mechanisms are discussed briefly.

Experimental data indicate that grain boundaries bear the primary responsibility for the weak link behavior observed in the high-temperature oxide superconductors.¹ However, neither the mechanism(s) by which grain boundaries limit the transport critical current density (J_{ct}) nor the specific features of the boundary which produce the weak link behavior have been identified. The detailed characterization of the structure, defect morphology, and composition of grain boundaries therefore remains of utmost importance. With this purpose in mind, high spatial resolution techniques such as energy-dispersive x-ray analysis (EDS) performed in the scanning transmission electron microscope (STEM)² and scanning Auger microanalysis of fracture surfaces^{3,4} have been used to investigate composition variations at $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries. Both types of experiments have indicated that, in general, the copper atom fraction is considerably larger and the oxygen atom fraction smaller at the boundary (i.e., within ~ 5 nm) than in the grain interiors. However, these studies have suggested that composition changes also occur within individual boundaries^{2,4} and from boundary to boundary.²⁻⁴ This letter presents direct evidence obtained by STEM EDS for regular composition variations within the boundary region.

Bulk samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were prepared by a grinding, mixing, and sintering technique.² Because these samples have a sharp inductive T_c ($\Delta T_c \sim 3$ K) and a low normal state resistivity ($\rho_n = 250 \mu\Omega \text{ cm}$ at 100 K), they are believed to be representative of good quality sintered material.⁵ The STEM specimens were prepared using two different techniques. Some specimens were mechanically dimpled to a thickness of $\sim 10 \mu\text{m}$ and then ion thinned to perforation with 4 kV Ar ions. The profiles in Figs. 1 and 2 were obtained from a specimen prepared in this manner. The remaining specimens were electropolished to perforation (3% perchloric acid in acetic acid, 13–15 °C) and ion thinned for a short time (30 min).

Only grain boundaries which were clearly free of second phase and structural defects in a diffraction-contrast image were chosen for study. (Suitable boundaries were readily identified in these samples since only a minority of the boundaries contained second phase.²) Their compositions were

investigated using a VG HB501 STEM (100 kV) equipped with an ultrathin window energy-dispersive x-ray spectrometer capable of detecting oxygen characteristic x rays. The microscope column was set up and aligned to produce an ~ 0.7 -nm-diam incident beam during the x-ray data acquisition. On the basis of the beam broadening formulation of Goldstein and Williams,⁶ the spatial resolution for composition determination was estimated to be in the range 5–8 nm for each of the profiles shown. Compositions were deduced by use of the standard thin-film analysis equations with k factors which were adjusted to give $\text{YBa}_2\text{Cu}_3\text{O}_7$ for the average composition of the grain interiors in each profile. In all figures, the concentrations of each element are given as atom fractions. The standard statistical analysis for x-ray spectroscopy⁷ suggested that the 99.7% confidence level oxygen precision was $\Delta\delta \sim \pm 0.45$. Since the yttrium, barium, and copper precisions are considerably better than this, the overall precision for composition determination is limited by the oxygen counting statistics.

Five of six composition profiles taken perpendicular to

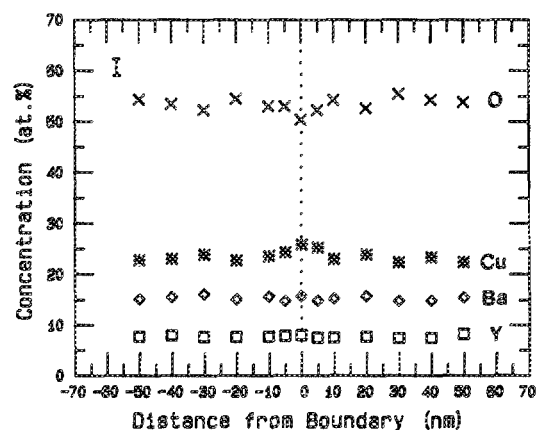


FIG. 1. Composition profile perpendicular to a grain boundary. Copper-rich zone is broadened to ~ 10 nm because boundary was slightly inclined to incident beam. 99.7% confidence level error bar for oxygen concentration determination is shown in corner of all profile figures. Error bars for other elements are one-quarter as large.

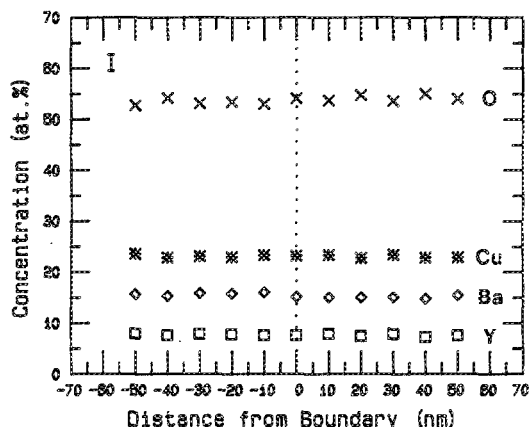


FIG. 2. Second composition profile obtained from same boundary as in Fig. 1, ~40 nm away.

four different boundaries showed the local (within ~5 nm) increase in copper atom fraction and decrease in oxygen atom fraction which was observed in previous studies²⁻⁴ (e.g., Fig. 1). The sixth profile (Fig. 2) showed no evidence of a composition change at the boundary, even though it was obtained only 40 nm away at the same boundary as the profile in Fig. 1. Thus, Figs. 1 and 2 give clear-cut evidence for composition variations within the boundary region. No evidence for an associated microstructural feature at the location of either profile was found in the diffraction contrast image.

In order to obtain a more detailed picture of the composition variations which are associated with individual grain boundaries, a composition profile was obtained along the boundary shown in Fig. 3, as well as perpendicular to it. The profile taken across the boundary (Fig. 4) again shows a copper-rich zone, which is atypically asymmetrical with respect to the boundary plane. As seen in Fig. 5, substantial, regular variations in composition were observed when the composition was profiled along the boundary. Pronounced oscillations in the copper, the yttrium, and to a lesser degree, the oxygen atom fractions were found to occur on a very

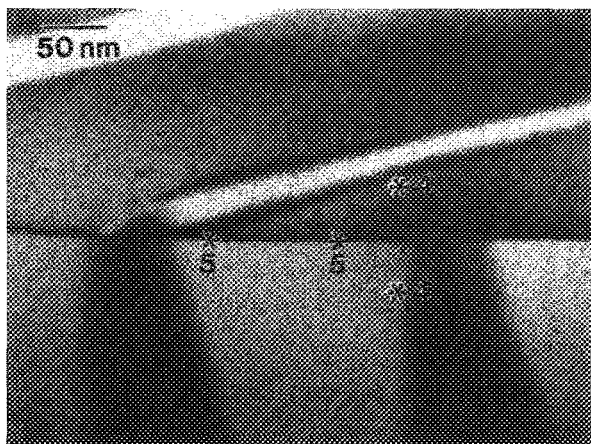


FIG. 3. Image of boundary from which profiles in Figs. 4 and 5 were obtained along lines between labeled asterisks. No evidence for second phase or defects at boundary is present.

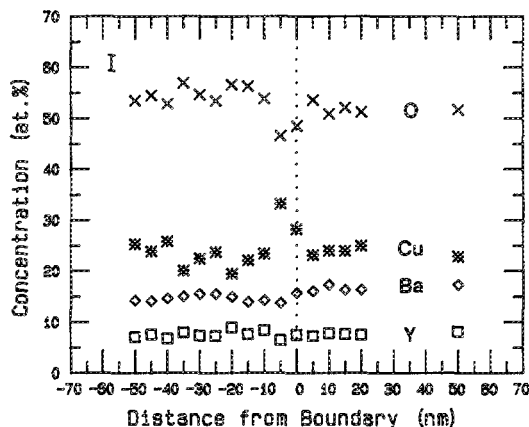


FIG. 4. Composition profile perpendicular to boundary shown in Fig. 3.

local scale (average peak-to-peak distance ~25 nm). Therefore, this example provides direct evidence for systematic composition variations both parallel and perpendicular to grain boundaries. A most notable feature of the composition variations observed within the boundary is their regular, oscillatory nature. This characteristic suggests strongly that the observed concentration variations are an intrinsic feature of the grain boundary. Evidence that the copper richness measured at grain boundaries is an intrinsic property has also been obtained in a previous study.³

The means by which the microstructure accommodates the observed composition variations is not clear. Diffraction contrast images of the grain boundary regions examined here showed no evidence of second phase, defects, or other features with the same spacing as the composition oscillations. However, some possible mechanisms by which excess copper atoms and periodic composition variations could be incorporated are suggested by prior studies. For example, the presence of $\text{YBa}_2\text{Cu}_4\text{O}_{8-\delta}$ has been revealed at specific grain boundaries by high-resolution microscopy techniques.^{8,9} It is quite possible that for some boundaries thin layers of this relatively copper-rich phase are responsible for the increased copper atom fraction which is observed. However, in contrast to the $\text{YBa}_2\text{Cu}_4\text{O}_{8-\delta}$ layers, which were imaged only on the surface of grains for which the *a-b* (bas-

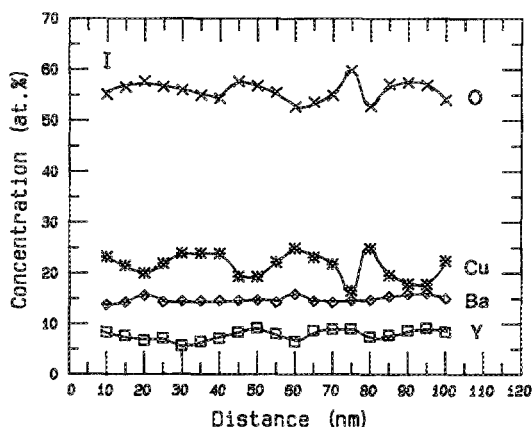


FIG. 5. Composition profile along boundary shown in Fig. 3 at position corresponding to $x = 0$ in Fig. 4.

al) plane is nearly parallel to the boundary,^{8,9} the present work shows copper-rich zones in boundaries which are not basal plane faced (for example, the asymmetrically copper-rich boundary of Figs. 3–5). Furthermore, it is unsatisfying to attribute the regular composition oscillations observed in Fig. 5 to a layer of the $\text{YBa}_2\text{Cu}_4\text{O}_{8-\delta}$ phase. An alternative possibility is that the regular composition variations are associated with the intrinsic grain boundary dislocation networks which have been observed in both high-angle¹⁰ and low-angle¹¹ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries. Segregation of impurity atoms to grain boundary dislocation cores has been observed directly by STEM in previous studies.^{12,13} Although grain boundary dislocation networks were not imaged in these particular boundaries, their presence could not be ruled out on the basis of the micrographs which were obtained.

The strong local composition variations observed within grain boundaries and the suggestion that subsections of the boundary have the same composition as the grain interiors prompt speculation concerning the means by which grain boundaries may limit J_c . It seems possible that local composition changes could reduce the grain boundary area through which supercurrent flows or produce microbridge behavior.^{14,15} Thus, the percolative character of supercurrent transport which has been suggested by a number of studies^{5,14–16} could be due to these local composition variations. Because the occurrence and scale of composition variations along the boundary may depend strongly on the boundary crystallography and sample history, experimental verification of these hypotheses presently seems to be a formidable research problem.

In summary, the present work has indicated that considerable variations in composition occur on a very local scale both parallel and perpendicular to grain boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. These results suggest that some regions of a given boundary may have the same composition as the abutting grains, yet the composition of other regions of the same boundary may deviate substantially from that of the grain interiors. The origins of the composition variations associated with grain boundaries are not presently understood, nor are their implications for electromagnetic properties. Nevertheless, it seems very reasonable to suggest that these varia-

tions could have a pronounced effect on the nature of electrical transport in polycrystalline high-temperature superconductors. From any view, however, the observations described here are indicative of the complexity of grain boundary structure and composition in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -type materials.

We gratefully acknowledge J. M. Seuntjens for bulk sample fabrication and J. L. Vargas and T. F. Kelly for discussions of the STEM data analysis. This work is sponsored by the Electric Power Research Institute and the U. S. Department of Energy—Division of High Energy Physics.

- ¹D. Dimos, P. Chaudhari, J. Mannhart, and F. K. LeGoues, *Phys. Rev. Lett.* **61**, 219 (1988).
- ²S. E. Babcock, T. F. Kelly, P. J. Lee, J. M. Seuntjens, L. A. LaVanier, and D. C. Larbalestier, *Physica C* **152**, 25 (1988).
- ³Y.-M. Chiang, J. A. S. Ikeda, and A. Roshko, in *Ceramic Superconductors*, edited by M. F. Yan (The American Ceramic Society, Westerville, OH, 1988), pp. 607–618.
- ⁴D. M. Kroeger, A. Choudhury, J. Brynestad, R. K. Williams, R. A. Padgett, and W. A. Coghlan, *J. Appl. Phys.* **64**, 331 (1988).
- ⁵D. P. Hampshire, X. Cai, J. M. Seuntjens, and D. C. Larbalestier, *Supercond. Sci. Technol.* **1**, 12 (1988).
- ⁶J. I. Goldstein and D. B. Williams, *Scanning Electron Microscopy/1977*, edited by O. Johari (ITRI, Chicago IL, 1977), p. 651–662.
- ⁷J. I. Goldstein, D. B. Williams, and G. Cliff, in *Principles of Analytical Electron Microscopy*, edited by D. C. Joy, A. D. Romig, Jr., and J. I. Goldstein (Plenum, New York, 1988), pp. 188–189.
- ⁸J. E. Blendell, C. A. Handwerker, M. D. Vaudin, and E. R. Fuller, Jr., *J. Cryst. Growth* **89**, 93 (1988).
- ⁹T. Kogure, Y. Zhang, R. Levonmaa, R. Kontra, W.-X. Wang, D. A. Rudman, G. J. Yurek, and J. B. Vander Sande, *Physica C* **156**, 707 (1988).
- ¹⁰S. E. Babcock, *Proceedings of the 46th Annual Meeting of EMSA*, edited by G. W. Bailey (San Francisco, San Francisco, 1988), pp. 622–623; S. E. Babcock and D. C. Larbalestier, *J. Mater. Res.* (unpublished).
- ¹¹M. F. Chisholm and D. A. Smith, *Philos. Mag. A* **59**, 181 (1989).
- ¹²E. A. Kenik, *Scr. Metall.* **21**, 811 (1987).
- ¹³J. R. Michael, C. H. Lin, and S. L. Sass, in *Proceedings of the 46th Annual Meeting of EMSA*, edited by G. W. Bailey (San Francisco, San Francisco, CA, 1988), pp. 612–613.
- ¹⁴D. C. Larbalestier, S. E. Babcock, X. Cai, L. D. Cooley, M. Daeumling, D. P. Hampshire, J. McKinnell, and J. M. Seuntjens, *Proc. Tokai University International Workshop on the Science of Superconductivity and New Materials*, edited by S. Nakajima (World Scientific, Singapore, 1989).
- ¹⁵R. Nicolsky, *Cryogenics* **29**, 388 (1989).
- ¹⁶T. Matsushita, B. Ni, and K. Yamafuji, *Cryogenics* **29**, 384 (1989).