Field ion microscopy of the polyphase structure of $YBa_2Cu_3O_{7-\delta}$

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The polyphase structure of this yttrium-based ceramic has been studied by field ion microscopy and mass spectrometry. Nanocrystalline structural features of two types have been observed. The dimensions of these structural features are much smaller than the thicknesses of the twin interlayers. It is suggested that these features are effective intragrain-pinning centers.

The low critical current densities of ceramic superconductors stem from the particular structure of the grain boundaries and from the nonsuperconducting atomic layers on these boundaries.[1] The superconconducting compound $YBa_2Cu_3O_{7-\delta}$ with $T_c=88$–93 K produced by the standard solid-phase synthesis method has a polyphase structure containing the 2-1-1 and CuO phases at a concentration of 2–10% by volume. It also contains a large number of twin interlayers.[2] Although twin boundaries are effective pinning centers if the magnetic field is oriented along the twinning interlayers, they could not, in general, be responsible for the observed intragrain pinning in ceramic[3] $YBa_2Cu_3O_{7-\delta}$. It is thus particularly important to carry out a microscopic analysis of the intragrain inhomogeneities with dimensions much smaller than the thicknesses of the twin interlayers, approaching the coherence length in order of magnitude. As was pointed out in Ref. 4, it is difficult to use diffraction methods to bring out features of the phase structure for dimensions at the nanometer range, because of interference effects. As a result, extremely little information is available on ultrafine-grain inclusions in yttrium-based ceramics.

In this letter we are reporting an analysis of the phase composition of the compound $YBa_2Cu_3O_{7-\delta}$ by the high-resolution methods of field ion microscopy and mass spectrometry.

Acicular samples with a tip diameter of 10–200 nm were prepared by electrochemical etching[5] from ceramic $YBa_2Cu_3O_{7-\delta}$ ($T_c=90$ K) produced by solid phase synthesis. After they were installed in the ion microscope and cooled to 80 K, the samples were cleaned by field desorption and formed by evaporation in an electric field of $(1–3)\times10^8$ V/cm. Nitrogen was used as the imaging gas. The mass spectrometry was carried out at 80 K in a field ion microanalyzer[6] with a mass resolution $M/\Delta M < 50$ and a spatial resolution of 1–3 nm. A two-pulse evaporation method made it possible to analyze a particularly clean surface.

Features of the structural and phase composition were distinguished by selective (preferential) field evaporation of nonaxisymmetric samples.[7] The tip of the point

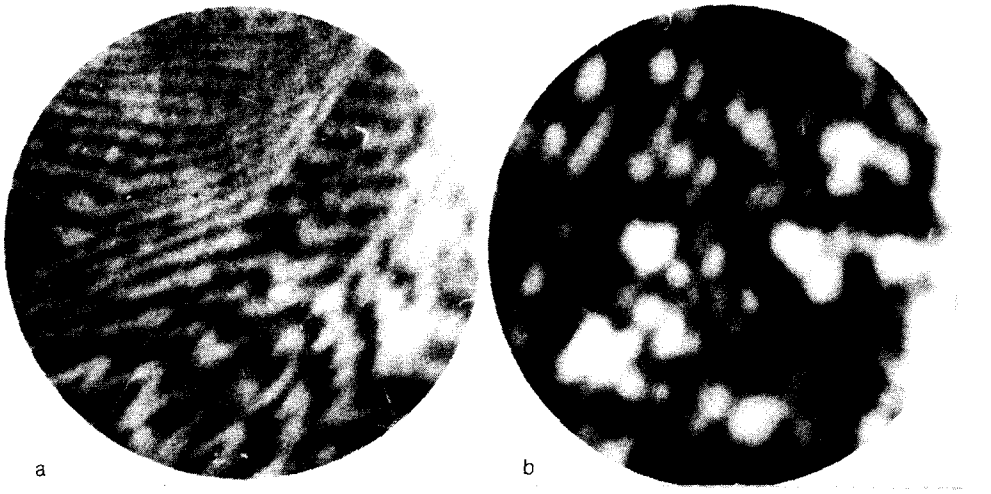


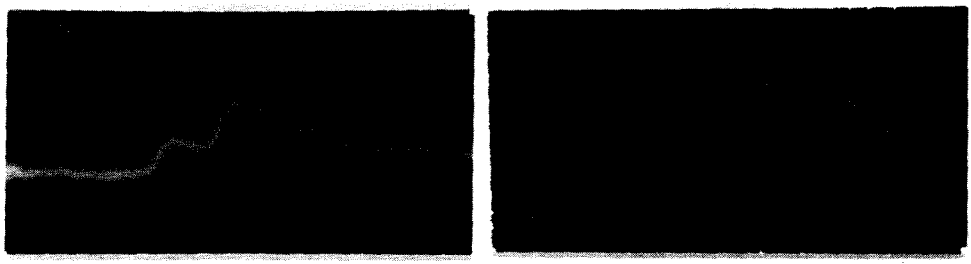
FIG. 1. Mass spectrograms of the field evaporation of ceramic YBaCuO. *a*—Matrix; *b*—CuO inclusions.

samples was an elliptical paraboloid with a semiaxis ratio $\theta = 5$–20. According to the results of Ref. 7, the changes caused in the major radius of curvature, R, by the preferential field etching and the corresponding local changes in the evaporating field E are related by

$$\Delta R/R = -(\Delta E_{ev}/E_{ev})\theta.$$

Since the smallest detectable value ΔR is constant and approximately equal to the resolution of the ion microscope (0.3 nm), the sensitivity of the method is proportional to the factor θ, which represents the deviation from axial symmetry.

A systematic analysis of ion-microscope images of this YBaCuO ceramic revealed microscopic inhomogeneities 2–4 nm in size. These inhomogeneities were detected on the basis of the local increase in image brightness. The regions with these microscopic inhomogeneities are distributed in a nonuniform way over the crystal. Their concentration reaches 2×10^{18} cm^{-3} in certain samples. The mass spectrometry also revealed regions which differ substantially in field-evaporation spectrum. The evaporation spectra of the ceramic are usually made up of O^+, Cu^{2+}, Y^{2+}, or Ba^{3+} ions. A layer-by-layer evaporation revealed regions whose evaporation spectrum can be represented by only two ion species: Cu^{2+} and O^+. The size of these regions along depth was a few atomic layers. Figure 1 shows the evaporation spectra of (a) the YBaCuO matrix and (b) of a region of two-component evaporation. Note that the mass spectrometry was carried out under conditions of multiparticle analysis, with several atomic layers being removed during each evaporating pulse. Since only two ion species were observed in this case, it can be concluded that the material contains microscopic inclusions of the CuO phase.



a b

FIG. 2. Ion-microscope images of (a) spherical particles and (b) nanodomains oriented along the {110} plane in the compound $YBa_2Cu_3O_{7-\delta}$.

The nonaxisymmetric samples revealed large regions with a layered structure (Fig. 2b). The layers were oriented normal to the (001) planes and were distinguished by virtue of a break on the projections of the (001) planes. The thickness of these layers ("nanodomains") varied from 2 to 20 nm, having an average value of 5 nm. This figure is one or two orders of magnitude smaller than the typical thicknesses of the twin interlayers. The structural width of the boundaries of the nanodomains is ~ 1 nm. Analysis of $\sim 10^2$ images showed that the boundaries of the nanodomains are not preferential sinks for point defects: There are no clusters of point defects or inclusions of second phases at them. The breaks in the (001) atomic planes observed at the boundaries are not associated with a change in the orientation of the layered nanodomains; they are instead a consequence of a change in the surface topography due to differences in the ease with which the layers are etched off by the field—a process which is intensified by the nonaxisymmetric shape of the samples. The complex ion-microscope image which results (Fig. 2b) is a consequence of the intersection of (001) planes with a surface having large variations in the local radii of curvature.

In some axisymmetric samples prepared from the same lot of yttrium ceramic, the layered nanodomains were not detected. The ion-microscope images are characterized by a high degree of regularity.[5] The reason why the nanodomains are "unobservable" in this case is the comparatively low sensitivity of the method of preferential field etching of axisymmetric samples (as discussed above). The fact that nanodomains are not observed is evidence that there are no important structural or orientational features at the boundaries of the nanodomains.

Mass spectrometry of both axisymmetric and axially asymmetric samples revealed no alternation of the mass spectra with a period greater than 5 nm. This result indicates that the chemical compositions of the nanodomains in contact with each other are the same, at least in terms of Y, Ba, and Cu. The different propensities of the nanodomains to undergo field etching is probably due to a difference in oxygen content, although this difference could not be detected unambiguously by the mass spectrometry.

In summary, microscopic structural features of two types have been observed in ceramic $YBa_2Cu_3O_{7-\delta}$: microscopic inclusions of copper oxides and large nanodomains oriented normal to (001) planes. The typical linear dimensions of the phases

which have been observed are considerably smaller than the average thicknesses of the twins and are comparable to the coherence length. These phases can thus be regarded as effective pinning centers.

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