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Author
Zandbergen, H.W.

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THE STRUCTURE AND PROPERTIES OF TWIN BOUNDARIES IN SUPERCONDUCTING YBa$_2$Cu$_3$O$_7$

H.W. Zandbergen$^+$, R. Gronsky$^+$, M.Y. Chu$^{++}$, L.C. DeJonghe$^{++}$, G.F. Holland$^{+++}$ and A. Stacy$^{+++}$

$^+$National Center for Electron Microscopy, and $^{++}$Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory, and $^{+++}$Department of Chemistry, University of California,
Berkeley, California 94720

ABSTRACT

A relationship between preparation procedures, diamagnetic yield and twin densities in YBa$_2$Cu$_3$O$_7$ has been established. Decreasing the calcination temperature causes an increase in the formation of [100] 90° rotation twins and a corresponding change in the c/a ratio. At sufficiently high densities of these twins, the tetragonal structure is stabilized. Correlations between c/a ratio and twin densities with the critical temperature and diamagnetic yield are reported.

INTRODUCTION

Following the discovery of YBa$_2$Cu$_3$O$_7$ as a high temperature superconductor, electron microscopy experiments revealed a considerable number of [100] 90° rotation twins in the microstructure of the early "as-produced" samples [1]. Across the boundary plane of these twins the c axis of the matrix continues as an a axis or b axis within the twin. Subsequent studies of specimens prepared under more carefully controlled conditions showed that these [100] 90° rotation twins were not present, raising the question whether or not the occurrence of the twins were due to irreproducible or uncertain details of the preparation procedure, for example, lax temperature control or variable stoichiometry.

X-ray powder diffraction from a mixture of Y$_2$O$_3$, BaCO$_3$ and CuO calcined at 850° C (to obtain a uniform YBa$_2$Cu$_3$O$_7$ compound for further sintering to high density materials [2]) showed almost no splitting of the 200, 020 and 006 reflections.
This calcined mixture was made in a quantity large enough to hinder oxygen uptake in the bulk upon rapid cooling; nevertheless, splitting of the 200 and 006 reflections should have been observed. It is also noted that such splitting was observed for YBa$_2$Cu$_3$O$_{7-\delta}$ calcined at 920°C and subsequently quenched from 800°C where YBa$_2$Cu$_3$O$_{7-\delta}$ is still in the tetragonal form.

Together these results suggested a correlation between the calcination temperature and the c/a ratio. Specifically, whenever the c/a ratio was very close to 3, it appeared that the formation of [100] 90° rotation twins was favored.

To investigate this hypothesis, a number of powder mixtures were calcined at various temperatures, and analyzed by X-ray diffraction, electron microscopy, and magnetic susceptibility measurements.

**EXPERIMENTAL PROCEDURES**

Samples were prepared from a single batch of thoroughly-mixed Y$_2$O$_3$, BaCO$_3$ and CuO powders by calcination at 790°C, 820°C, 850°C, 880°C, and 910°C for 50, 24, 12, 6, and 3 hours, respectively.

Magnetic susceptibility measurements were made using a SHE SQUID magnetometer at 12.5G. The magnetic field was calibrated by measuring the magnetization of a superconducting Sn sphere at liquid He temperature.

For the electron microscope investigations, powdered material was suspended in ethanol. A few droplets of the suspension were put on a carbon-coated Triafoil™ holey film spanning the openings of a Cu grid. When thoroughly dry, the suspension yielded a large number of thin supported particles suitable for study in the transmission electron microscope. Specimens were placed into the microscope immediately to prevent decomposition [4]. High resolution electron microscopy was carried out in a JEOL JEM 200CX electron microscope, equipped with top-entry ±10° double-tilt goniometer and operating at 200 kV.

**EXPERIMENTAL RESULTS**

X-ray powder diffraction data are shown in Figure 1. It is evident that there is...
a strong correlation between the calcination temperature and the splitting of the 200 and 006 reflections. The unit cell parameters and the c/a ratio as a function of the calcination temperature are given in Table 1.

Magnetic measurements made on samples that were post-annealed at 450° C for 1 hour show a large dependence of the magnetic properties on calcination temperature. These results are shown in Figure 2. At calcination temperatures of 850° C and above, the onset of the transition to superconductivity is approximately 90 K with a width of as much as 50 K. At calcination temperatures of 820° C or lower, the onset of superconductivity is at a much lower temperature, i.e., about 30 K. Over the whole range of calcination temperatures, the diamagnetic yield decreases strongly with a reduction in calcination temperature.

X-ray powder diffraction shows the samples calcined at 820° C or below to contain detectable amounts of BaCuO₂. The intensities of the BaCuO₂ reflections as well as the peak-to-background ratio of the YBa₂Cu₃O₇₋δ reflections show that at least 75% of the material is YBa₂Cu₃O₇₋δ. Consequently, the difference in diamagnetic yield cannot be simply explained by differences in sample purity.

High resolution electron microscopy and electron diffraction show that with decreasing calcination temperature the number of [100] 90° twins increases. An example is given in Figure 3. It is difficult to quantify the density of twins, since the twin density varies significantly from sample to sample. Nevertheless, a definite trend was observed. For specimens calcined at 880°, 850°, 820°, and 790° C, the twin density per μm³ had approximate values of 0, 2, 5, and 10 respectively.

**DISCUSSION**

Lower calcination temperatures increase the probability of the formation of [100] 90° rotation twins having twin boundaries that are predominantly (100) planes. It is noted for comparison that the phase transition from tetragonal (high temperature) to orthorhombic (low temperature) structures always leads to the formation of another type of twin, a [110] mirror twin, in which the a and b axes
are interchanged across the twin boundary. Such twins are formed to accommodate the strain energy of the tetragonal-to-orthorhombic transformation, by alternating directions of the different-length crystalline axes across the twin boundary planes.

The presence of pre-existing [100] 90° rotation twins in the tetragonal phase has significant implications. When the transition to the orthorhombic phase occurs, such twin boundaries should act as impediments to the complete transformation of the high temperature phase. This is due to the fact that the transformation twins would be unable to cross the [100] 90° rotation twin boundaries because of the incompatible crystallography at the intersecting interfaces. The required strain energy will at least reduce the free energy decrease accompanying the tetragonal-to-orthorhombic transformation, and might completely inhibit the transformation for sufficiently high [100] 90° rotation twin densities.

In the present study, there was a striking difference between samples calcined at about 800°C (and subsequently cooled rapidly to room temperature) and those prepared above 900°C, then annealed at 800°C (followed by the same rapid cooling to room temperature). For the first group of samples, the c/a ratio is very close to 3, whereas for the latter the c/a ratio is about 3.06. In-situ neutron powder diffraction at 820°C of YBa$_2$Cu$_3$O$_{7-δ}$ powder calcined at 925°C also confirmed a c/a ratio of 3.06 [5]. Figure 1 clearly shows that the 800°C calcined samples in this study exhibited changes in both the a and the c axes. This differs from another neutron diffraction study [6] of YBa$_2$Cu$_3$O$_{7.3}$ in which a c/a ratio = 3 was attributed to a decrease in the just the c axis.

This difference in c/a ratio can be explained in two ways. First, at temperatures of about 800°C, multiply-twinned material is formed and the existence of these twins restricts the c/a ratio to be very close to 3. Second, because of structural differences in those samples calcined at temperatures around 800°C compared to those calcined above 900°C, the c/a ratio is again restricted to be very close to 3. These structural differences can arise from a number of causes: (i) a
higher oxygen content in the lattice; (ii) partial disordering of the Ba and Y sites; or (iii) partial occupation of oxygen vacancies. However, some of these possibilities can be eliminated.

Partial disorder among the Ba and Y cations would lead to a decrease in scattered x-ray intensities of hkl reflections having \( l \neq 3n \), since the deviation from the cubic perovskite structure is manifested predominantly in the intensities of these reflections. However for the samples studied in this work, there were no significant changes in relative intensity between those reflections of the class \( l \neq 3n \) (e.g. 005, 104, and 014) and those of the class \( l = 3n \) (e.g. 113). It is therefore unlikely that the observed difference is caused the disordering of Ba and Y. Also, since oxygen in the CuO plane at \( z = 0 \) is very mobile, it is unlikely that the observed \( c/a \approx 3 \) is caused by a higher oxygen content in the CuO plane at \( z = 0 \). Another possible way to trap oxygen inside the structure is to locate it within the Y plane at \( z = 1/2 \), pointing to need to conduct more careful experiments on oxygen stoichiometry.

ACKNOWLEDGEMENTS

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REFERENCES

Figure captions

Fig. 1. X-ray diffraction pattern of YBa$_2$Cu$_3$O$_7$, obtained by calcination at 910°C (full line) and 790°C (dashed line).

Fig. 2. Magnetic susceptibility data of the powders calcined at 790°, 850° and 910°C and post-annealed at 450°C.

Fig. 3. High resolution image of YBa$_2$Cu$_3$O$_7$ showing strong twinning. In region "A" the c axis is normal to the projection, in region "B" it lies in the projection horizontally, and in region "C" it is vertically oriented.
Fig. 1

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Fig. 2 XBL 8711-4631