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Materials Analysis of Yttrium-Barium-Copper-Oxide by Micro-Raman Spectroscopy and Optical Microscopy

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Abstract— Optical microscopy has proven to be a useful technique for obtaining general, qualitative information from the entire surface of YBa$_2$Cu$_3$O$_{7-z}$ samples. Micro-Raman spectroscopy is well suited for routine microstructural analysis of YBCO superconductors. We demonstrate the complementary use of both techniques for the analysis of polycrystalline YBCO. Observed colors of polarization on YBCO were correlated with information provided by Raman spectroscopy on individual grains to deduce microstructural characteristics across the whole surface of a sample.

I. INTRODUCTION

In addition to chemical composition, the electrical properties of bulk, superconducting YBa$_2$Cu$_3$O$_{7-z}$ (YBCO) are determined by the material’s microstructure. Granular size, orientation, chemistry, the presence of texture, composition of grain boundaries, and impurities, all affect electrical properties such as critical current density [1]. It is therefore important to understand the microstructure of YBCO when considering the properties of specific materials. Ideally one would like to determine the distribution of microstructural properties throughout a sample. Raman spectroscopy and optical microscopy are two common methods for characterizing superconducting ceramics. Each technique is able to determine certain characteristics which the other cannot.

Raman spectroscopy, and especially Micro-Raman spectroscopy (MRS), may be applied to the analysis of YBCO. In a Raman experiment, one usually detects the five vibrational modes with $A_g$ symmetry. These modes involve atomic vibrations parallel to the long axis (the c axis) of the YBCO unit cell [2]. They occur at 118, 150, 335, 435, and 505 inverse centimetres, or wavenumbers (cm$^{-1}$) (labelled here A-E, respectively). Of these, two modes producing Raman spectral peaks near 335 cm$^{-1}$ and 505 cm$^{-1}$ (peaks C and E, respectively) are particularly sensitive to microstructural factors such as oxygen stoichiometry ($7-z$) and the orientation of YBCO crystals with respect to the polarizations of the incident and scattered laser beams. The peak near 505 cm$^{-1}$ (peak E) is from the vibrations of the O(4) atoms toward the Cu(1) atom, parallel to the c axis. It is most strongly detected when the polarizations of the incident and scattered radiation are parallel to each other and parallel to the c axis. This peak is much more weakly detected for polarizations where the incident and scattered radiation are perpendicular to the c axis. The position of this peak has a linear variation with $7-z$ [3], and the detected position is often used to provide a measurement of $7-z$.

Another peak of interest (peak C), near 335 cm$^{-1}$, is from the out-of-phase, bond-bending motion of the O(2) and O(3) atoms. This peak is detected only for radiation polarizations perpendicular to the c axis. This peak also has an intrinsic, Fano-like asymmetry due to the interference between the phonon mode and the background continuum of electronic excitations [4]. We have found that it may be possible to measure $7-z$ in a region of irradiated YBCO from the asymmetry of this peak [5].

YBCO displays characteristic colors when viewed through crossed polarizers. When observed through crossed polarizers and a first-order red tint plate, orthorhombic YBCO appears blue or yellow; whereas tetragonal YBCO appears the same color as the tint plate (magenta), even when the sample is rotated [6]. Other groups have observed the same color changes in samples transforming from orthorhombic to tetragonal [7], [8]. A further development of this phase-analysis method has revealed that when a YBCO sample is illuminated by light from a xenon lamp and examined through crossed polarizers, characteristic colors are observed at room temperature: golden for orthorhombic YBCO and greyish brown for tetragonal YBCO. The golden color exists for samples where $7-z \geq 6.5$. As $7-z$ decreases, the yellow component gradually disappears [9]. The colors are the result of YBCO’s optical properties, which are determined by crystal structure and oxygen stoichiometry.

Many groups have employed Raman spectroscopy to characterize YBCO materials [10], [11]. However, a microstructural analysis by MRS on polycrystalline YBCO, on a grain by grain basis, has not yet appeared. MRS analysis of YBCO has the disadvantage that it is a micro-

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scopic technique, Obtaining information from a large surface by this technique requires the collection and analysis of many spectra, especially if the sample surface is untextured. On the other hand, optical microscopy analysis surveys a whole sample surface, providing general phase information and assisting the identification of texture. Microscopy, however, provides only a general identification of phases without a precise measure of stoichiometry and grain orientation. In this study, we have investigated how MRS and optical microscopy analysis of YBCO could be correlated and used together.

II. Experimental Procedure

One sample of bulk, polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ was examined in this study, produced by thermal spraying as described elsewhere [12], [13]. The onset transition temperature as determined by AC susceptibility was 90.3 K. At 77 K, the critical current density, $J_c = 65$ A/cm$^2$. From X-ray diffraction (XRD) analysis it was determined that the bulk oxygen stoichiometry, $7 - x = 7$.

The sample was mounted, polished, and etched [14] for microscopy analysis. An examination in bright field revealed the grain structure. We selected 15 grains and grain boundaries for MRS experiments. Both black-and-white and color micrographs were obtained from the sample in crossed polarized light. We used an Olympus metallurgical microscope, equipped with a polariser, an analyser, and a first-order red tint plate. The polariser and analyser directions were kept at right angles, and color micrographs were obtained with and without the tint plate. Perpendicular directions X and Y were defined on the sample to form reference coordinates for the MRS experiments.

The micro-Raman experiments were performed at room temperature by means of a Dilor Microdil 28 micro-Raman spectrometer in backscattering geometry [15]. The incident laser light (of wavelengths 4880 or 5145 Å) was linearly polarised in either the X or Y direction at the sample. We did not use an analyzer to select the polarization of the scattered radiation. The polarisations selected for the spectra are thus defined as $(X)$ and $(Y)$. The empty space in the notation indicates the absence of the analyser in the scattered beam. The Raman microscope produced a spot size on the sample less than eight microns wide, allowing us to collect data from individual grains. We determined peak positions and oxygen stoichiometry by means of the technique described previously [5].

III. Results

Figure 1 is a representative micrograph of the sample, while it was illuminated by polarized light. The grains were largely rectangular in shape, having a longest dimension of 80 microns or less. When color micrographs were obtained, the optical anisotropy of most grains was visible. Many grains displayed a color shift away from the magenta of the tint plate towards either yellow or blue. The same grains exhibited the opposite shift when the sample was rotated 90°. When the tint plate was re-
moved, many grains had a bright yellow to white color at low magnification. Other grains appeared dark without the tint plate, and magenta with the tint plate. They were in an orientation necessary for extinction. If the sample was rotated by 45°, these same grains were no longer extinct. In general, the optical effects were most apparent at lower magnifications.

Based on the color techniques described earlier, microscopic observation indicated that most of this sample was orthorhombic YBCO. The varying colors and contrasts among the grains suggested that any overall texture on the sample surface was minimal. However, when the tint plate was inserted, collections of grains were visible with the same color and contrast to neighboring grains for all rotations of the sample and all positions of the polariser.

One group of such grains (positions 1, 12, 14, 15) was examined by MRS. Twinning was also visible in most grains. In those few grains which showed a criss-cross twin pattern, color shifts to cream and to blue were visible within the grains.

A close examination of this sample in bright field without the polariser, analyser, and tint plate revealed numerous white deposits at the grain boundaries, non-uniformly distributed throughout the sample surface. The contrast between these white deposits and the surrounding grains was much greater when viewed in bright field than when viewed through crossed polarizers. We collected a spectrum from one such deposit at position 10.

Some of the grains selected for MRS experiments, and the directions X and Y are labelled in figure 1. Representative spectra are shown in figures 2 to 5. Stars mark the positions of spurious emission lines in the Raman data [16]. Figures 2-5 indicate that all five $A_g$ peaks were detected in the spectra. The peaks' varying relative intensities point to the random orientation of the grains. The spectra from positions 1, 12, 14, and 15 confirm their common orientation, which was suggested by their polarization colors. The spectrum from position 10 confirmed that the white deposits were CuO. Table 1 summarizes both the optical anisotropy of the grains examined and quantitative information for this sample, concerning peak positions and oxygen stoichiometry.

IV. DISCUSSION AND CONCLUSION

The spectra and the micrographs indicate that the grains in both samples were randomly oriented. Most of the grains in the sample were orthorhombic. The spectra and the micrographs did reveal some tetragonal YBCO. The sample microstructure is consistent with its high transition temperature and low critical current density. The value of $T - 2$ as determined from the spectra was in agreement with the color of the corresponding grain. The spectra could also be used to determine the orientation of a given grain and evaluate texture among groups of grains. We were able to identify which grains had a similar orientation, and this similarity was confirmed by the corresponding spectra.
In previous work, similar thermally sprayed samples have been identified as having superconductor-insulator-normal-superconductor junctions at the grain boundaries [17]. The presence of CuO at the grain boundaries was due to the addition of excess copper in the precursor powders, and this excess copper promoted the growth of large grains [12].

The combination of optical microscopy with MRS is superior to the collection of many spectra to obtain an indication of the distribution of phases, oxygen chemistry, grain orientation, and impurities in a sample. This technique would be especially useful in the analysis of YBCO films, allowing a determination of epitaxy and stoichiometry over a large area.

In conclusion, MRS can be effectively applied to the study of YBCO on a granular level. The grains need to be larger than the diameter of the incident laser beam so that the experiment samples an individual grain. The analysis needs to be supplemented with another technique so that the spectra may be interpreted in the light of the microstructure of the entire sample. Through MRS analysis, the observed colors of polarization for orthorhombic and tetragonal YBCO were calibrated, and a correlation has been demonstrated between micro-Raman spectroscopy and optical microscopy analysis. The two methods are complementary.

REFERENCES