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Ion-channeling study of single-crystal $YBa_2Cu_3O_x$

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We have performed Rutherford backscattering spectroscopy and axial ion channeling on superconducting single crystals of $YBa_2Cu_3O_x$. Single-crystal platelets with dimensions of more than 2 mm along the *a* and *b* axes were prepared by a partial-melt growth technique. Angular profiles of the channeling yield and surface-peak intensities were measured individually for Y, Ba, Cu, and O. A minimum yield of 3.5% for channeling of 1.66-MeV He^+ ions along the *c* axis was observed on a crystal with an area of 0.5 mm^2. Analysis of the results demonstrates that the crystallinity and stoichiometry of the as-grown samples is quite good to within about 1 nm of the surface. The surface-peak intensities indicate surface disorder equivalent to roughly one molecular monolayer. The surface order is quite insensitive to prolonged exposure to room air.

INTRODUCTION

Our knowledge of the structural, chemical, and physical properties of the recently discovered high-temperature superconductors[1,2] has developed at an unprecedented rate. Nonetheless, a number of important experiments are awaiting the availability of single crystals of suitable size and quality. Recent advances[3-5] have made it possible to grow single-crystal platelets of $YBa_2Cu_3O_x$ with dimensions of several millimeters along the *a* and *b* axes.

Rutherford backscattering spectrometer (RBS) provides an absolute, quantitative compositional analysis of surfaces, and is particularly well suited for the analysis of compounds containing heavy elements. In the axial channeling mode, RBS is sensitive to long-range crystalline order and provides a depth-dependent measure of crystal defects.[6] We have performed a RBS and channeling study of the surface crystallinity and stoichiometry, and the amorphization and annealing behavior of $YBa_2Cu_3O_x$. Our results show that the bulk crystal structure and cation stoichiometry are present within a nanometer of the as-grown crystal surface. This information on the surface quality is of considerable significance for other experiments utilizing surface-sensitive techniques, such as electron spectroscopies, to probe these crystals.

The ability to perform channeling allows the quantitative study of the effects of various surface processing techniques on the crystal structure and composition, and this work provides a reference point for such studies. Preliminary results have been obtained on annealing of 100-nm amorphous layers formed on the surface of single crystals by 30-keV oxygen-ion implantation, and will be reported elsewhere.[7] We expect that RBS channeling will contribute significantly to an understanding of the thermal and chemical stability of interfaces between the oxide superconductors and the substrates, overlayers, and ambients with which they come in contact.

EXPERIMENTAL PROCEDURES

Single crystals of $YBa_2Cu_3O_x$ were grown using a nonstochiometric melt-growth technique similar to that reported in Refs. 3-5. X-ray powder diffraction measurements of representative crystals confirmed the expected perovskite structure, and superconducting onset temperatures of about 90 K in unannealed samples were determined by diamagnetic susceptibility measurements. The crystals grew as (001)-oriented platelets up to 0.4 mm thick and 3 mm along the *a* and *b* axes. The (001) faces of the platelets were often free of visible defects over areas of 1-4 mm^2. These defect-free areas, when examined under polarized light, were also generally found to be free of microscopic twin boundaries where the *a* and *b* axes are exchanged. Because of the nature of the growth technique, however, the crystals were sometimes attached or embedded in a polycrystalline matrix, limiting the yield of large, free crystals.

Single crystals with mirrorlike surfaces were bonded to low-atomic-number substrates (Be, C, Al, Al_2O_3, or Si), rinsed in methanol, and mounted on a precision dual-axis goniometer for RBS analysis. The samples were stored in desiccators, but had been exposed to room air for 1-50 h without obvious effects on the surface structure. Crystal faces were aligned at right angles to the He beam using the back reflection of a collinear laser beam. Channeling and RBS measurements were made in an ultrahigh vacuum chamber with a well-collimated beam of 1.66- or 3.05-MeV He ions. The beam size was adjusted in each case to cover the entire crystal. The energies of He ions backscattered at 165° were measured by a Si surface-barrier detector. Simulations of idealized RBS spectra generated by the program RUMP (Ref. 8) were used for comparison to normalized experimental data. Measurements of the oxygen composition and channeling yields were effectively impossible using ordinary RBS, since the O signal rides on a large background and is comparable to the statistical noise. However, we were able to observe channeling effects in the oxygen sublattice using a nuclear resonance at 3.045 MeV to enhance the oxygen backscattering yield.[9]

RESULTS AND DISCUSSION

In Fig. 1 we compare a ⟨001⟩-aligned channeling spectrum, an unaligned spectrum, and a simulated spectrum

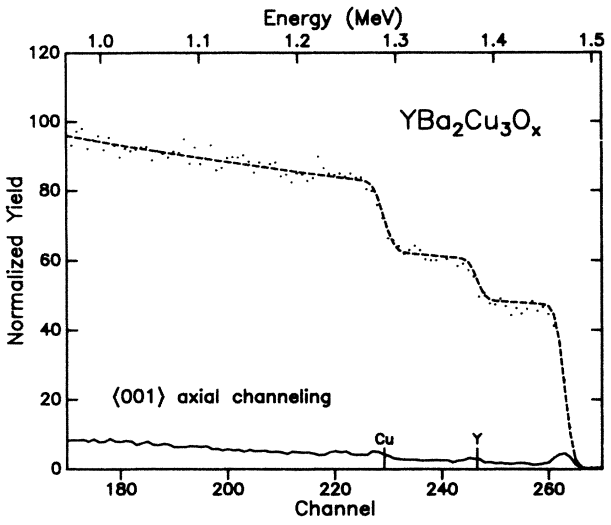

FIG. 1. Unaligned and channeling RBS spectra of single-crystal $YBa_2Cu_3O_x$ taken at 1.66-MeV incident He-ion energy. The unaligned spectrum is plotted as points and is overlaid with a simulated spectrum (dashed curve).

for the nominal $YBa_2Cu_3O_7$ stoichiometry. The rightmost edge is due to surface backscattering from the heaviest constituent element Ba and the energies for the surface backscattering from Y and Cu are indicated by tick marks. The corresponding energy for oxygen backscattering is 0.6 MeV. The simulated spectrum incorporates only two adjustable parameters, the experimental energy resolution and the vertical scale. The close agreement with the unaligned spectrum indicates that this crystal has nearly a 1:2:3 cation stoichiometry right to the surface, although a deficiency of up to 2% in the Ba yield was seen in some crystals.

The aligned channeling spectrum shows a dramatic reduction in the total backscattering yield and three small peaks attributable to surface backscattering from the three cations. Viewed along the ⟨001⟩ direction, the $YBa_2Cu_3O_x$ structure consists of a YBa_2 atom row, a Cu_3O_2 row, and two O_{2+y} rows per unit cell. The amplitudes of the surface peaks provide a measure of the absolute density of atoms exposed to the incident He beam because of the surface termination of the atom rows, enhanced static and vibrational displacements of atoms from the rows near the surface, and surface disorder.[6] Ignoring scattering by oxygen for the moment, the ideally terminated (001) crystal at 0 K would yield surface amplitudes corresponding to one Cu atom and one Y or Ba atom per surface unit cell (depending on plane of surface termination). At room temperature, the measured surface scattering occurs in roughly the bulk stoichiometric ratio. The surface scattering intensity is equivalent to about 1×10^{15} cm^{-2} $YBa_2Cu_3O_x$ molecules, implying that there is only about one monolayer (6.7×10^{14} cm^{-2}) of misregistered molecules at the crystal surface. The measured surface disorder is not correlated with exposure to room air. Not all samples displayed nearly ideal channeling, but of 14 crystals which showed channeling, none have shown surface-disorder peaks substantially larger than those in Fig. 3.

The quality of the bulk crystal is reflected in the low level of the aligned yield. Following the model of Barrett,[10] we estimated the minimum aligned backscattering yield for Ba in a perfect crystal would be 3.2% of the unaligned yield. Therefore, the observed minimum yield of 3.5% indicates nearly ideal channeling. The low surface and bulk backscattering yields demonstrate the high degree of order and lack of mosaic spread and strain in this crystal over its entire surface area of 0.8×0.6 mm^2. We note, however, that *c*-axis channeling will not reveal *a-b* twinning, nor can it be used to distinguish between the orthorhombic and tetragonal phases of the compound.

Another measure of the crystalline quality is obtained by analyzing the angular dependence of the backscattering yield near the channeling direction. To obtain the angular profile of the Ba channeling yield, we took RBS spectra at various tilt angles about the ⟨001⟩ axis, then integrated the Ba signal over a 0.05-MeV interval below the surface peak. The Cu and Y signals ride on a background of approximately exponential form[10] due to backscattering from heavier elements. After correcting for this back-

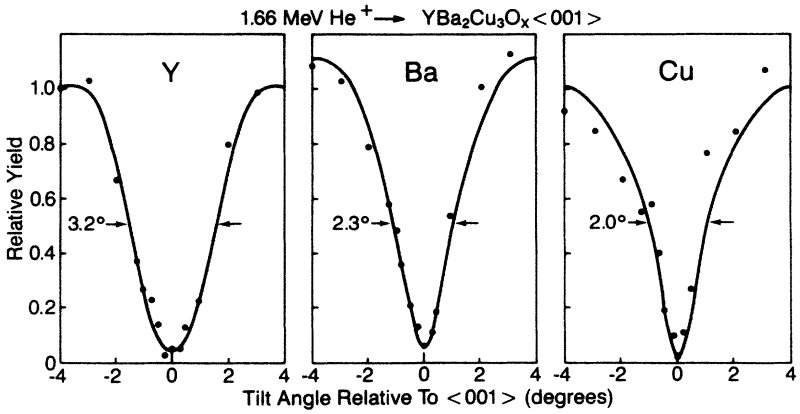

FIG. 2. Bulk backscattering yield as a function of tilt angle for Y, Ba, and Cu. Yields are normalized to the random unaligned yield. Smooth, symmetrical curves have been drawn through the points.

ground, the angular dependences of Y and Cu backscattering yields were also estimated from the RBS spectra. The resulting angular channeling profiles are presented in Fig. 2, normalized to the yields from an unaligned RBS spectrum. Symmetrical curves have been drawn through the data to emphasize the differences in the angular width of the profiles.

The solid angle of acceptance for axial channeling is roughly proportional to the atomic number. Therefore, the oxygen minimum yield is the most sensitive indicator of crystalline quality, and low minimum oxygen channeling yields cannot be reliably measured even in crystals with low minimum yields for cation channeling. In Fig. 3 we present a 3.05-MeV channeling spectrum which shows channeling in the oxygen sublattice. The dashed curve is a simulated spectra for the nominal $YBa_2Cu_3O_7$ composition which is based upon the Rutherford cross section, and does not include nuclear resonance effects. Sharp peaks occur in the actual RBS spectra because the oxygen backscattering cross section is enhanced as the He ions are slowed through the resonance energy (3.045 MeV) at a depth of about 50 nm below the surface. This enhancement makes an accurate quantitative study of the oxygen backscattering possible. The oxygen resonance peaks in Fig. 3 include a substantial contribution from surface oxygen in the Be substrate. The magnitude of this substrate signal could be estimated by measuring the nominal oxygen yield from a larger ceramic sample. The angular profile of the oxygen channeling dip is shown in Fig. 4, and an estimate of the substrate background is given by the dashed line.

The quality of the channeling in these crystals decreases with time as a consequence of ion beam damage. We find that a He-ion dose of the order of 1×10^{17} cm^{-2} causes the cation minimum yields to increase by about 5% over the initial yields. In order to collect the spectra from which Fig. 2 is derived, fluences of this magnitude were required, and the data are affected accordingly.

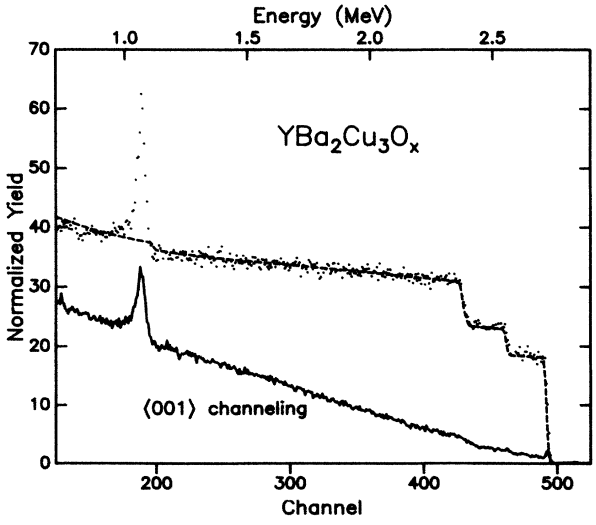

FIG. 3. Unaligned and ⟨001⟩-aligned RBS spectra taken at 3.06-MeV He-ion energy. The simulated spectrum (dashed curve) is not corrected for the oxygen backscattering resonance which occurs near channel 190.

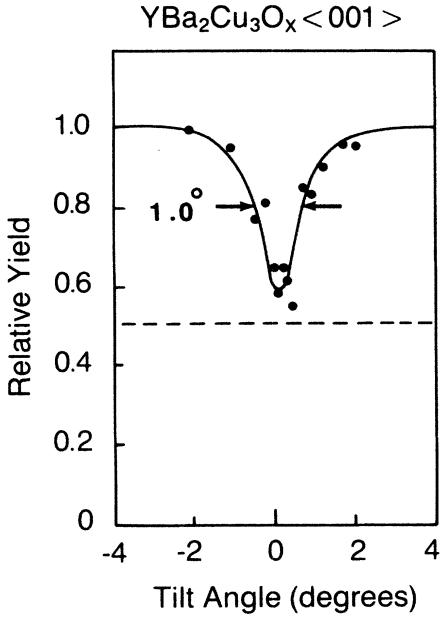

FIG. 4. Oxygen resonance yield as a function of the tilt angle from the ⟨001⟩ axis. The dashed line is an estimate of the background yield due to substrate O.

CONCLUSIONS

Our bulk channeling results agree well with expectations for high-quality crystals based on the crystal structure and lattice dynamics of $YBa_2Cu_3O_x$ derived from neutron-diffraction studies.[11,12] On the other hand, the thinness of the disturbed surface layer that we observe on the as-grown crystal faces was somewhat unexpected. We emphasize that no surface preparation other than methanol rinsing was performed on these crystals and that they were exposed to humid air, in some cases for days, yet the equivalent surface disorder was always less than 2 nm and the surface stoichiometry was nearly ideal. This calls into question the moisture sensitivity originally attributed to this material, and demonstrates that the (001) face of single crystals is quite stable and unreactive.

A general theory of channeling yields in multielement crystals has not been developed. Therefore, we have calculated the angular widths of the channeling dips at the appropriate energies using analytical expressions derived for simple elemental crystals.[10] These results should be valid for the atoms which are in single-element atomic rows (oxygen in the two O_{2+x} rows) and for the heavier elements in the compound rows (Ba in the YBa_2 rows and Cu in the Cu_3O_2 rows). Using average isotropic temperature factors reported in neutron-diffraction studies,[11,12] the calculated angular widths at half height for Ba, Cu, and O are, respectively, 2.02°, 1.60°, and 0.76°. The measured angular widths given in Figs. 2 and 4 are about 0.3° larger. This discrepancy may be due to the simplicity

of our calculations, or may reflect some slight mosaic spread or bowing of the crystals.

Since the electrostatic repulsion of the atom rows is the underlying mechanism of ion channeling, the narrower channeling widths for Cu and O are to be expected on the basis of the lower electrostatic potential of the Cu_3O_2 and O_{2+x} atomic rows relative to the YBa_2 row. Thus, the flux of He ions will be larger near the Cu and O nuclei at small tilt angles, increasing their backscattering probabilities. On the other hand, since Y and Ba lie along the same ⟨001⟩ atomic rows, the He flux distribution near their lattice sites is quite similar. The dramatic difference between the Y and Ba profiles is therefore attributed to shadowing of the Y atoms by the neighboring, heavier Ba atoms with correlated lateral vibrations.

The dynamics of the Cu-O layers and the effects of oxygen vacancies on high-temperature superconductivity have attracted considerable theoretical and experimental attention. The structure of the oxygen sublattice is clearly a central issue in these materials. Many diffraction experiments have been conducted to determine the structural parameters of the oxygen atoms. RBS channeling is potentially very sensitive to the dynamic and static displacements of the oxygen from their ideal lattice sites, since (unlike diffraction probes) out-of-row atoms are emphasized in a channeling spectrum. The utility of channeling measurements for the study of Jahn-Teller and charge-density-wave phase transitions has already been demonstrated.[13,14] The temperature dependence of channeling profiles on high-quality crystal of varying oxygen content should provide useful insights into the structural properties of this high-temperature superconductor.

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