Top-Seeded Melt-Growth of YBa$_2$Cu$_3$O$_x$ Crystals for Neutron Diffraction Studies

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We have grown cubic centimetre-size crystals of YBa$_2$Cu$_3$O$_x$ suitable for neutron studies, by a top-seeded melt-growth technique. Growth conditions were optimized with an eye toward maximizing phase purity. It was found that the addition of 2% Y$_2$BaCuO$_5$ and 0.5% Pt (by mass) were required to prevent melt loss and to obtain the highest crystallinity. A neutron diffraction study on a mosaic of six such crystals found that the final Y$_2$BaCuO$_5$ concentration was 5%, while other impurity phases comprised less than 1% by volume. The oxygen content was set to $x = 6.5$, the crystals were detwinned and then carefully annealed to give the well-ordered ortho-II phase. The neutron study determined that 70% of the mosaic’s volume was in the majority orthorhomic domain. The neutron (0 0 6) and (1 1 0) rocking curve widths were $\sim 1^\circ$ per crystal and $\sim 2.2^\circ$ for the mosaic, and the oxygen chain correlation lengths were $> 100$ Å in the $a$- and $b$-directions and $\sim 50$ Å in the $c$-direction.

Keywords: crystal growth, top-seeded melt-growth, Ortho-II, YBCO, neutron scattering

1. MOTIVATION

Neutron scattering is an extremely powerful technique for investigating spin fluctuation and magnetic ordering in superconducting samples. However, to obtain reasonable signal to noise one requires sample sizes on the order of several cubic centimetres. The self-flux technique,$^{1, 2}$ which produces the highest-quality YBa$_2$Cu$_3$O$_x$ single crystals and is the primary method for growing crystals for fundamental research, has thus far only been able to yield crystals as large as 5 mm $\times$ 5 mm $\times$ 5 mm. Additionally, YBa$_2$Cu$_3$O$_x$ is difficult to grow in an image furnace, due primarily to the low solubility of Y$_2$BaCuO$_5$ in the BaO-CuO melt.$^{3}$

The top-seeded melt-growth technique has been widely used to grow YBa$_2$Cu$_3$O$_x$ crystals as large as several inches in diameter$^{4, 5, 6, 7, 8, 9, 10, 11}$, but these crystals were in-plane. Meanwhile, our study determined that 70% of the mosaic’s volume was in the majority orthorhomic domain. The crystals were then annealed to the oxygen-ordered ortho-II phase. The neutron yield crystals as large as 5 mm. Addition-

2. CRYSTAL GROWTH

Precursor YBa$_2$Cu$_3$O$_x$ and Y$_2$BaCuO$_5$ powders were made by preparing stoichiometric mixtures of Y$_2$O$_3$ (99.999% pure), BaCO$_3$ (99.999%) and CuO (99.995%), then calcining in BaZrO$_3$ crucibles at $\sim 950^\circ$C until the reaction was complete as determined by X-ray diffraction. The YBa$_2$Cu$_3$O$_x$, Y$_2$BaCuO$_5$ and Pt powders were mixed in an agate mortar under ethanol, then pressed in a cylindrical mold under 300 MPa of hydrostatic pressure. The resulting pellet was approximately 13 mm high by 12 mm in diameter, and had a mass of $\sim 10$ g.

The addition of a small amount of Pt$^{12}$ is required to prevent melt loss during growth by increasing the melt’s viscosity. We found that $\frac{1}{2}$% Pt by mass was required for this purpose. Without the addition of Y$_2$BaCuO$_5$, the crystals were porous, had poor mosaic spread, and contained BaO-CuO flux inclusions. Best results were obtained when the pellet contained 2% Y$_2$BaCuO$_5$ by mass.

A higher concentration of Y$_2$BaCuO$_5$ was found to be necessary for proper seeding, so a small quantity of Y$_2$BaCuO$_5$-rich powder (10% Y$_2$BaCuO$_5$ by mass) was added to the top of the pellet prior to pressing. This layer constituted $\sim 0.4$% of the pellet.

NdBa$_2$Cu$_3$O$_x$ was chosen as a seed crystal for its near-perfect lattice match and for having a melting temperature $\sim 80^\circ$C higher than that of YBa$_2$Cu$_3$O$_x$. The seed and pellet were placed on a disc-shaped substrate, loaded into a three-zone vertical tube furnace, and subjected to the temperature program shown in figure 2. After a sintering step at 990°C, a temperature gradient of $\sim 5^\circ$C was applied and the pellet was melted, then slowly cooled. This effectively moved the peritectic temperature

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Through the pellet, from seed to substrate, over the course of several days.

While several substrates were tested, including alumina (Al₂O₃) and single-crystalline MgO and SrTiO₃, satisfactory results were only obtained using BaZrO₃ discs.

The top of each crystal had an elevated Y₂BaCuO₅ concentration and often extraneous domains near the edge, while the bottom had a layer with a high concentration of impurity phases which had been pushed there by the growth front (including much of the platinum). The top and bottom millimetres of the crystal were accordingly cut off using a diamond saw. Additionally, a millimetre was removed from two opposite sides, to create flat (1 0 0)/(0 1 0) faces for detwinning. We were able to align the crystals visually to within a degree.

To form the oxygen-ordered ortho-II phase of YBa₂Cu₃O₆.₅, which has alternating full and empty chains, the oxygen content was set to \( x = 6.53 \) by annealing for one week in 1 atm oxygen gas, at 760.0°C, in the same conditions as for single crystals [13]. It has been reported that the ortho-II phase’s longest oxygen correlation lengths may be realized at oxygen contents slightly above 6.50 [14].

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FIG. 1: The crystallization furnace program, where \( T_s \) is the average temperature of the pellet and \( t \) is the time. The inset depicts the growth setup, showing the geometry of the pellet, seed, and substrate.

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Further neutron scattering results will be published elsewhere [13].

3. ANALYSIS

Magnetization measurements in a Quantum Design SQUID magnetometer found the crystals’ \( T_c \) to be 59 K, and 2.5 K wide (field-cooled, \( H = 1.5 \) Oe, \( H \parallel \hat{c} \)).

A sample was subjected to EDX compositional analysis to determine the shape and distribution of impurity phases. Y₂BaCuO₅ was only observed at the base of the pellet, near the growth front, but the equipment’s ~1 μm resolution makes it insensitive to small inclusions in the bulk. Two Pt-containing phases were found, one of which was consistent with the formula Y₂PtBa₃Cu₂O₁₀. Neutron scans found weak impurity peaks consistent with this compound as well.

Neutron diffraction experiments were carried out at the NRC Chalk River laboratory (NRU reactor). There, six crystals were sealed in airtight cans under dry helium, aligned, and inserted into the E3 spectrometer. The (0 0 0.6) and (1 1 0) rocking curve widths were ~1° for each crystal, and ~2.2° for the mosaic of six. Figure 3 shows ortho-II ordering superlattice diffractions via radial scans through (\( \frac{1}{2} a^* 0 0 \)) and (0 0 \( \frac{1}{2} a^* 0 \)). The detwinning was incomplete – the majority domain occupied only 70% of the sample volume. The neutron study also found that the concentration of Y₂BaCuO₅ in the mosaic was ~5% by volume, while all other impurity phases constituted less than 1%.

A determination of the oxygen ordering correlation length was resolution limited (horizontal bar in figure 3), but a fit to a resolution-convolved Lorentzian indicated a length >100 Å in the a- and b-directions and ~50 Å in the c-direction. Given the growth method used, these compare remarkably well with the values of \( \xi_a = 148 \) Å, \( \xi_b = 430 \) Å and \( \xi_c = 58 \) Å obtained in high-purity single crystals [13]. Indeed, they even exceed the correlation lengths found in many flux-grown single crystals.

Further neutron scattering results will be published elsewhere [13].
4. CONCLUSION

We have grown and detwinned cubic centimetre-size crystals of ortho-II \( \text{YBa}_2\text{Cu}_3\text{O}_6.5 \), with oxygen ordering correlation lengths \( >100 \, \text{Å} \) in the plane and \( \sim 50 \, \text{Å} \) in the \( c \)-direction. They contain \( 5\% \) \( \text{Y}_2\text{BaCuO}_5 \) by volume and are partially detwinned, with \( 70\% \) of their volume in the major orientation. Each crystal has a rocking curve width of \( \sim 1^\circ \). These crystals are currently being studied in detail by neutron scattering, and have already shown that their symmetry is not broken by satellite Bragg peaks associated with static long-range d-density wave order, as is seen in less-ordered crystals [15].

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