Growth of YBa$_2$Cu$_3$O$_y$ single crystals from a mixture of YBa$_2$Cu$_3$O$_y$ and Ag$_2$O

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Single crystals of the superconductor YBa$_2$Cu$_3$O$_y$ have been grown from a mixture of solid phase YBa$_2$Cu$_3$O$_y$ and liquid phase silver. Crystals with a thickness of up to 1 mm along the c axis can be obtained when the mixture is soaked at 1005 °C for more than 8 h. Silver melt enhances the peritectic partial melting of the YBa$_2$Cu$_3$O$_y$ solid phase, and induces the solution and reprecipitation process during sintering at 1005 °C. Stacked plate-like YBa$_2$Cu$_3$O$_y$ grains grow through a coalescence process. Crystals are heavily twinned after 20 h of O$_2$ annealing at 500 °C. They exhibit a sharp superconducting transition with an onset temperature of 93 K in zero field.

Since the first observation of the levitation effect in samples of YBa$_2$Cu$_3$O$_y$/Ag$_2$O composites, considerable efforts have been devoted to the flux pinning and mechanical workability enhancement in these composites. Thermal studies indicated that the addition of silver enhances the phase stability of the high T$_c$ superconducting oxide and limits the oxygen out-diffusion.2 The results also suggested that larger grain growth of YBa$_2$Cu$_3$O$_y$ (Y-123) and fine precipitation of silver at the grain boundaries might be responsible for the observed enhancements. Recently, we have developed a process to grow high J$_c$ superconducting Y-123 crystals from a mixture of stoichiometric Y-123 and Ag$_2$O without the introduction of any unwanted flux materials.3 The crystals thus prepared are plentiful and large in three dimensions. The crystals are also heavily twinned and contain many imperfections. Magnetic hysteresis measurements show that the critical current density of the crystal at 1 T is $\sim 2 \times 10^4$ A/cm$^2$.

Stoichiometric Y-123 powder was mixed with a 99.5% pure Ag$_2$O powder (> 180 μm) at the weight ratio of 3 to 1. The well-mixed powder was pressed into the form of a disk (1 mm thick, 10 mm in diameter) under 3 tons/cm$^2$ pressure. Each pellet was laid flat on top of a gold foil in an alumina crucible and then introduced into a furnace with disk (1 mm thick, 10 mm in diameter) under 3 tons/cm$^2$ pressure. The specimens were initially sintered at 950 °C for 6 h, then slowly heated to 1005 °C. Exaggerated grain growth of Y-123 occurred after 8 h at this temperature. The specimens were cooled at a rate of 6 °C/h to 950 °C and held there for 6 h. They were then slowly cooled to 500 °C and held there for 20 h for oxygen uptake before they were cooled to room temperature.

Small facet-like Y-123 grains were formed on the surface of the pellet during the sintering at 950 °C. The silver particles resulted from the dissociation of Ag$_2$O distributed primarily at pores, and densified the pellet. Silver beads began to form on the surface of the pellet as the specimen was heated to a temperature above 980 °C. No conspicuous grain growth could be seen for the initial few hours of sintering at 1005 °C. Energy-dispersive x-ray (EDX) analysis of the whole specimen showed that a small amount of the Y$_2$BaCuO$_5$ phase and Ag-rich particles dispersed in the grain or at grain boundaries. BaO-CuO flux resulting from partial melting of Y-123 was extruded out of the grain and distributed at the pores. Most of the silver particles became embedded in the flux, reacted with Ba-Cu-O, and formed a complex network structure. As the sintering time at 1005 °C increased to more than 8 h, large and stacked plate-like Y-123 crystals appeared. Crystals were randomly distributed on the surface of the pellets, as shown in Fig. 1. The microstructural analysis shows that Ag and Ba-Cu-O melts were distributed at grain boundaries and grain corners. Some of the Ag-rich small particles and Y$_2$BaCuO$_5$ precipitates were trapped in the grains or in the facet grain boundaries, because they were unable to diffuse out in time while plate-like grains rapidly contacted each other and coalesced.4 Most of the Ag and Ba-Cu-O melts percolated through the compact and reacted with the gold foil underneath it. Except for a small amount of Ba-Cu-O melt remaining in voids, some Ba-Cu-O of the melt was extruded to the sample surface and reacted with the Y$_2$BaCuO$_5$ phase and Ag-rich particles, which act as nucleation and growth centers, resulting in a hilllock-shaped microstructure [Fig. 1(b)]. EDX analysis indicated that most hillocks were Y-123 phase with an excess of yttrium. Well stacked plate-like grains were arranged in the a-b direction, and increased in size by further coalescence and growth processes.4 Within a single domain, slight misorientations ($< 2^\circ$) between the stacked grains were observed with an x ray precession camera (MoKα radiation) (Fig. 2). Single crystals of $3 \times 2 \times 1$ mm$^3$ in size can be grown using this technique with $\sim 16$ h of soaking at 1005 °C. Cube-like crystals up to a thickness of 1 mm were easily removable by breaking the pellet apart with tweezers. Some crystals are shown in Fig. 3.

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FIG. 1. (a) Typical SEM micrograph of the top surfaces of the as-grown YBa$_2$Cu$_3$O$_y$ crystals obtained from a liquid phase sintering of a thin pellet of a mixture of YBa$_2$Cu$_3$O$_y$ and Ag$_2$O. The largest crystal seen here is approximately 3 × 2 × 1 mm$^3$. (b) The top surfaces of crystals are full of hillocks or ripples. EDX analysis indicated that most of the hillocks are Y-113 phase with an excess of yttrium.

FIG. 2. Photograph of the diffraction pattern taken with an x-ray precession camera with the incident beam parallel to the c axis of a crystal. Small-angle misorientations (< 2°) between the stacked grains were observed.

Y-123 crystals grown from this technique are heavily twinned after 20 h of O$_2$ annealing at 500 °C (during cooling) and typically yield a sharp superconducting transition (with a width of less than 0.5 K) at an onset temperature of ~93 K. These crystals also exhibit attractive forces in a magnetic field oriented both normal and tangential to their surfaces. The superconducting resistive transition in magnetic fields applied parallel to the c axis of the single crystal is broadened, but still exhibits zero resistance above 70 K in a field of 15 T (Fig. 4). This observation suggests strong flux pinning in these crystals. The resistive transition in the fields shows clearly the "resistive knee," which has also been observed in single crystals grown by the conventional flux method, but two such anomalies are observed. Preliminary studies suggest that the appearance of the resistive knee is intrinsic and may be related to the dimensional cross over of the flux motion. Details of the results will be
reported in the near future. The magnetic hysteresis, measured in a Quantum Design superconducting quantum interference device (SQUID) magnetometer at 77 K gives a critical current density of \( \sim 2 \times 10^4 \text{ A/cm}^2 \) at 1 T based on the Bean's critical state model. Large domains of Y-123 consist of stacked grains with low crystallographic misorientation \( \text{Y}_2\text{BaCu}_3\text{O}_y \) and Ag-rich fine particle precipitates are dispersed evenly in the grain or at the low-angle grain boundaries, contributing to flux pinning and resulting in the enhancement of the critical current density.

In conclusion, the addition of \( \text{Ag}_2\text{O} \) in the stoichiometric Y-123 powder is very effective in obtaining superconducting Y-123 crystals. Silver may enhance the peritectic partial melting of Y-123 and act as an accelerator of the coalescence of the grains. Large and plentiful single crystals of mm size in three dimensions can be obtained. These crystals contain many imperfections, such as small-angle grain boundaries of less than 2', microcracks from thermal strains and a small amount of inclusions of residual solids.

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