Characteristics and growth of single crystals of $Y_1Ba_2Cu_3O_7$ with superior microwave properties

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We report the fabrication and high-frequency characterization of single crystals of $Y_1Ba_2Cu_3O_7$ with extremely sharp microwave transitions. The 10 GHz surface resistance R_s is less than 400 $\mu\Omega$, at temperatures 4 K below the transition temperature. The electrodynamic characteristics of these crystals were examined via several measurements, and we demonstrate that high quality crystals which show very low R_s also possess small penetration depths $\lambda(0) = 1600$ Å and small magnetic field effects on the penetration depth characterized by $k(0) \equiv (d\lambda/dB^2)_{T\to 0} = 10^{-3}$ Å/G^2. In polycrystals, and even in poor single crystals, the presence of Josephson junctions of typical effective area $\sim 4\ \mu m^2$ leads to poor microwave properties, with electrodynamic parameters orders of magnitude larger.

The intense scrutiny of the recently discovered oxide superconductors clearly reveals that proper control of fabrication procedures is essential to realizing the great potential in improved performance expected of these materials, both as regards applications and in understanding the intrinsic properties. A particularly important area of applications is at microwave frequencies, and microwave studies show that poor performance, reflected in large values of the surface resistance R_s, is the norm. Despite the large number of microwave studies,[1-4] a comprehensive picture which can account for the observed behavior is yet to be achieved. In fact, even phenomenological correlations have not been established. This letter reports the fabrication of high quality single crystals of $Y_1Ba_2Cu_3O_7$ and their high-frequency characterization, and also identifies and correlates measured electrodynamic parameters.

We have synthesized single crystals of $Y_1Ba_2Cu_3O_7$ which display extremely sharp transitions and superior transport characteristics at microwave (10 GHz) and radio frequencies (1–10 MHz). We have characterized these crystals by a variety of measurements: temperature dependence of the surface resistance $R_s(T)$ at 10 GHz, and temperature and field dependence of the penetration depth $\lambda(T,B)$ at 1–6 MHz. The R_s and λ of the high quality single crystals decrease dramatically faster below T_c than for polycrystalline samples, and also in comparison to most single crystals and thin films. Our measurements of R_s show a sharp drop within 4 K below T_c. At lower temperatures R_s is less than 400 $\mu\Omega$, which represents the limit of our sensitivity for small crystals (although we employ one of the most sensitive techniques currently available). At 6 MHz, the rf transition widths are <0.2 K, in contrast to polycrystalline samples which have widths of about 4 K and other single crystals which have widths between 0.5 and 2 K. These experiments enable us to determine the electrodynamic parameters of the high quality crystals and compare them to polycrystals (see Table I). A clear correlation is seen between the various parameters, with the best crystals possessing small $\lambda(0)$, $d\lambda/dB^2$, and R_s, in contrast to the poor quality samples. We identify the polycrystalline response as due to Josephson junctions of characteristic size $\sim 4\ \mu m^2$, whereas in the best single crystals, the effective junction area determined from our experiments is less than $0.025\ \mu m^2$.

From a long process of trial and error, we conclude that fabrication procedures have to be tightly controlled for both the preparation and subsequent annealing, in order to achieve superior microwave properties. Improper annealing conditions yield crystals with broad transitions and poor response. Apparently proper annealing of improperly prepared crystals also yields poor quality crystals. While these conclusions may appear to be obvious, the parameter space within which high quality crystals can be produced is extremely restricted, and in this work, we have been able to achieve the optimum conditions required.

The crystals were grown from the eutectic melt.[5] A mixture of prereacted $Y_1Ba_2Cu_3O_7$ and $BaCO_3$ and CuO powders was thoroughly mixed and placed in a ZrO_2 crucible. The nominal composition of the mixture was $Y_1Ba_4Cu_{10}O_7$. The mixture was ramped to 1000 °C with a ramping rate 5 °C/min, soaked at 1000 °C for 30 h, followed by a slow cooldown with a ramp rate less than 0.1 °C/min. We have found that it is important to keep temperature fluctuations to less than ± 0.5 °C. Several single crystals were found in the solidified mass, particularly near voids. These were extracted very carefully by simple mechanical means. As-grown crystals usually do not show any sign of superconductivity at 77 K, as determined from a levitation test. Crystal sizes vary typically from 0.5 to 4 mm^2, and recently we have obtained crystals of size 2×3 mm^2.

The crystals were annealed in flowing oxygen at temperatures between 450 and 600 °C for periods in excess of a week. After annealing, the crystals clearly show superconductivity, and were used for the measurements reported here.

We have found that ZrO_2 crucibles give better results than Al_2O_3 and MgO. Although ZrO_2 does react with the melt and contaminates crystals which grow near the crucible wall, crystals obtained from the center of the crucible are almost contamination free. The crystals were examined with both a scanning electron microscope and a polarized optical microscope. The scanning electron microscope reveals extremely smooth surfaces, and when examined on a broken edge, also shows a step-like morphology. The composition was found to be $Y_1Ba_2Cu_3O_{7-\delta}$. Whereas for poor quality crystals the polarized light microscope showed a grid-like structure attributable to twin boundaries of typical dimen-

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sions 20 μm square, the high quality crystals do not show this structure. (We do not rule out the existence of twin boundaries, but qualitatively the twin density is much less than for poor crystals.)

We note that the high quality crystals typically possess lower T_c's (75–87 K). In our experience thus far, crystals with T_c's of 93 K have shown poor microwave properties. However, these results do not preclude the preparation of crystals with T_c's of 93 K and with superior microwave properties. Perhaps even longer annealing periods are necessary to achieve higher transition temperatures. We emphasize that the value of T_c does not appear to be a determining factor as regards microwave performance; rather the relevant parameters are those listed in Table I.

We have found that the visual appearance of the crystals is a good guide to the microwave properties. Crystals which possess smooth, shiny surfaces and have a rectangular plate-like morphology have superior microwave properties. As an example, one of the crystals was cleaned with heptane, upon which the surface shine was found to degrade, resulting in a very broad transition and poor R_s. The importance of the surface is understandable, since the penetration depth is of order 10^3 Å, and the superconductor has to maintain ideal properties over this length near the surface.

Since the primary object of this work is to understand and improve the microwave response in relation to synthesis procedures, we have focused on correlating the electrodynamic properties, particularly the surface resistance (at 10 GHz) and the penetration depth (at 10 GHz and 4–6 MHz). The penetration depth is especially important, since although the primary requirement for applications is low values of R_s, the penetration depth strongly determines R_s, and can set limits on it. (This can be understood, for example, for conventional s-wave superconductors, where in the local limit, $R_s \propto \lambda^{3/4}$ for $T \ll T_c$.) We find that the structural and chemical characteristics are not yet an adequate guide to the microwave response; in fact, the latter is a much more sensitive probe of sample quality.

The 10 GHz R_s measurements were carried out using the technique of Ref. 6, with a superconducting cavity made of Nb or Pb-plated Cu maintained at 4.2 K and the sample temperature variable between 4.2 and 150 K. This method for R_s is currently one of the most sensitive available, for small samples. The rf measurements of λ were carried out with resonant coils.[7] In the rf experiments, changes of λ, viz. $\Delta\lambda(T,B)$, were measured both as functions of temperature and magnetic field.

The behavior for R_s with temperature is shown in Fig. 1, for the high quality single crystals of this work, and also for polycrystalline samples. To date we have measured a variety (over 50) of samples in ceramic, thin film or single crystal forms, which usually display poor results. These earlier samples were either synthesized by us, or obtained from other laboratories, thus encompassing a variety of fabrication procedures. The polycrystal results shown in Fig. 1 can be regarded as representative of most "garden variety" samples.[1,8]

In contrast, the single crystals reported here show a quantum improvement in performance, as is obvious from Fig. 1. The absolute magnitudes of R_s were cross-checked by calibration runs with Cu samples of the same nominal dimensions as the crystals. The normal state R_s of the high quality crystals is below that of the other samples. This is due to a lower normal state resistivity, which is estimated using the classical skin depth result as 25 $\mu\Omega$ cm from $R_s = 0.1\ \Omega$ at T_c, in comparison to normal state values of 369 $\mu\Omega$ cm and 0.37 Ω for polycrystalline samples. The low values of the normal state resistivity is also indicative of the sample quality.[9] From the normal state values, R_s drops within 4 K below T_c to values less than 400 $\mu\Omega$, which is the upper limit of our sensitivity since the sample is very small (0.5 $mm^2 \times 40$ μm thick). It is obvious from the results that the crystal R_s is substantially below that of Cu.

The radio-frequency characteristics of all samples correlate well with the microwave measurements. The high quality samples, which show superior microwave performance, also display very sharp radio-frequency transitions, as shown in Fig. 2. Typical transition widths, defined as 10–90 % of the total frequency shift from $T \gg T_c$ to $T \ll T_c$, are

TABLE I. Comparison of measured electrodynamic parameters for polycrystal and single-crystal $Y_1Ba_2Cu_3O_7$.

Sample	ΔT_c[a] (K)	$\lambda(0)$[b] (Å)	$k(0)$[c] (Å/G^2)	R_s (4.2 K)[d] (Ω)
Polycrystal (unoriented)	7	7.5 μm	160	5×10^{-3}
Poor single crystal	3	8500	0.07	N/A
Better single crystal	0.5	2000	0.03	N/A
Best single crystals	<0.2	1600	10^{-3}	$\ll 400\times10^{-6}$

[a] Determined from inductive transitions at 4–6 MHz.
[b] At 4–6 MHz. For single crystals the rf magnetic field is perpendicular to the c axis.
[c] Determined from 4–6 MHz data with a dc magnetic field, where $k = d\lambda / dB^2$. Both the dc and rf fields are perpendicular to the c axis.
[d] From 10 GHz superconducting cavity measurements.

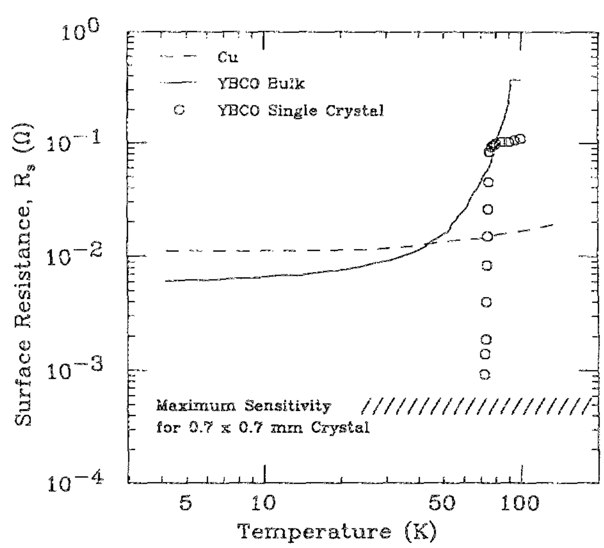

FIG. 1. Surface resistance R_s vs temperature at 10 GHz, for polycrystals and high quality single crystals.

about 7 K for polycrystals, 0.5–3 K for poor quality single crystals, and <0.2 K for the high quality single crystals. (See Table I.) (The inductive transition widths are to be distinguished from the dc resistivity transition widths, which are much sharper, e.g., 0.5 K for the polycrystal.)

The penetration depth of the samples can be determined from the frequency shift data using the relation $\Delta\lambda = -G\Delta f$, where G is a geometric factor. For the high quality crystal, the data are in good agreement with a two-fluid Gorter–Casimir behavior, from which we also extract a zero-temperature penetration depth $\lambda(0) = 1600$ Å. In fact such fits are themselves a measure of sample quality.[10,11]

It is important to note that, in contrast, poor quality samples show large penetration depths (of order microns) at all temperatures, with zero-temperature values of $\lambda(0) \approx 7.5$ μm. This is indicated in Table I, where it is apparent that the polycrystals which have poor R_s also possess very large $\lambda(0)$. It is important to point out that even nominal crystals possess large $\lambda(0)$, which can vary between 2000 Å and 1 μm, and are hence classified as poor quality.

The temperature dependences of R_s and λ, although they show strong correlations and are important parameters in assessing high-frequency performance, do not point toward a microscopic mechanism for the wide variation in the observed properties. An experiment which is a very sensitive test of sample characteristics is the study of the dependence of the penetration depth on a static magnetic field. This field was perpendicular to the c axis of the sample. Experimentally, for fields $H < H_{c1}$, λ is found to increase quadratically with field, i.e., $\Delta\lambda(T,B) = k(T)B^2$. Polycrystalline samples show a huge dependence characterized by $k(0) \equiv (d\lambda/dB^2)_{T\to 0} = 160$ Å/G^2. In an earlier paper,[7] we have shown that these large values can only be understood in terms of Josephson junctions. It can be shown[7] that the Josephson penetration depth varies with field quadratically, given by $k(0) = (\pi^2/24)\lambda(0)(\Sigma/\phi_0)^2$, where Σ is the effective junction area and ϕ_0 is the flux quantum unit. In the polycrystals, the results of the experiment lead to typical junction areas of $\sim 4\ \mu\text{m}^2$. As Table I shows, it appears that these junctions are present even in nominal crystals, as they have appreciable values for the quadratic coefficient $\approx 10^{-1}$ Å/G^2.

In contrast, the high quality single-crystal samples show very weak effects five orders of magnitude smaller, viz. $k(0) = 10^{-3}$ Å/G^2. The results of this experiment indicate that the role of the junctions is greatly minimized or probably absent in single crystals. An upper bound on the junction area using the above model is 0.025 μm^2. (The data for the single crystals are in good agreement with a Ginzburg–Landau model of the intrinsic response.) It is evident from the table that the values of $k(0)$ and $\lambda(0)$ correlate well with each other and with the microwave results.

In summary, we have successfully fabricated high quality crystals with superior microwave properties, and have correlated the microwave response with other electrodynamic parameters. The single-crystal results may indicate a lower limit to the surface resistance determined by the intrinsic mechanism for superconductivity, while the polycrystalline results suggest an extrinsic mechanism which we show to be attributable to the presence of Josephson junctions.[7,12] Further analysis of the temperature dependence of the electrodynamic parameters and the relation to microscopic theories is the subject of a separate publication.

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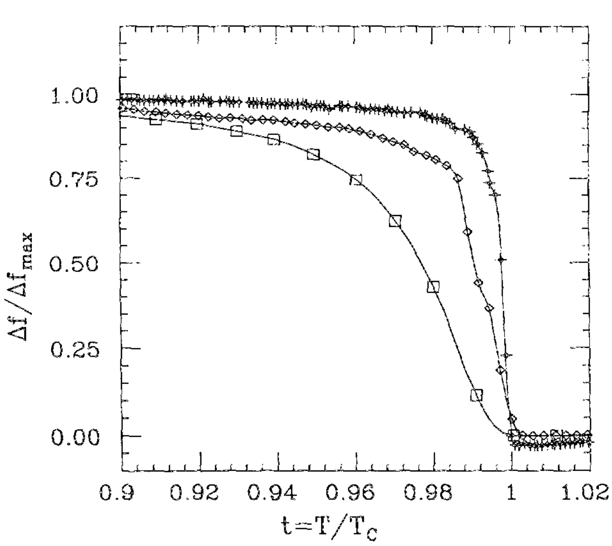

FIG. 2. Normalized inductive frequency shifts vs reduced temperature for a polycrystal (squares), a poor single crystal (diamonds), and a high quality crystal (+).

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