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SYNTHESIS, OXYGEN TREATMENT AND AC SUSCEPTIBILITY STUDIES OF YBaCuO SINGLE CRYSTALS

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We describe the procedures we are using for synthesizing and characterizing YBaCuO single crystals. Results of an oxygen annealing study of thicker crystals prepared elsewhere are also reported.

In this paper we describe the procedures we have been using recently to prepare and characterize single crystals of superconducting yttrium barium copper oxide. Following several reports in the literature /1/ we are using alumina crucibles and excess barium and copper oxide to produce a low melting point flux for crystal growth. Thin (10-100 μm) high quality single crystals are necessary for studying the magnetic field penetration depth in the superconducting state /2/ as well as transport properties and critical currents in the a-b plane.

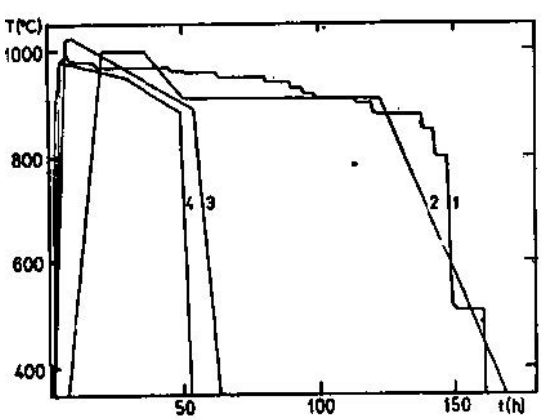

Figure 1

The starting compositions tried until now are given in the table I, and corresponding temperature-time profiles in Figure 1. "Johnson Matthey" chemicals of 99,9% purity were used and charges of 8-10 gms. In order to avoid problems with decomposing $BaCO_3$ we often started with barium nitrate produced from a known weight of $BaCO_3$.

An A.D.A.M.E.L. (Paris) tubular furnace was used throughout.

STARTING MATERIAL	CATION RATIO	CRUCIBLE	TEMP. FIG 1	CHARACTERIZATION
Y_2O_3	1:14:35	ALUMINA*	4	GOOD CRYSTALS, T_c=81 K+
		ALUMINA	1	NO CRYSTALS, FLUX CREEP
		ALUMINA LINED WITH Pt FOIL	1	NO CRYSTALS, FLUX REACTS WITH Pt FOIL
		ThO_2 COATED ALUMINA	4	NO CRYSTALS
$Ba(NO_3)_2XH_2O$	"	Au EVAPORATED ALUMINA	1,2	GOOD CRYSTALS, T_c=75 K+
		Au PLATED ALUMINA 12 um	4	GOOD CRYSTALS, T_c=52 K+
CuO	2:14:35	Au EVAPORATED ALUMINA	1	GOOD CRYSTALS, T_c=60 K+
	3.5:14:35	Au PLATED ALUMINA 12 um	4	NO CRYSTALS
Y_2O_3	3.5:14:35	ALUMINA	3	NO CRYSTALS, FLUX CREEP
		ALUMINA LINED WITH Pt FOIL	2	NO CRYSTALS
$BaCO_3$ CuO		Au EVAPORATED ALUMINA	3	SMALL CRYSTALS, BAD MORPHOLOGY

* ALUMINA MADE IN LJUBLJANA FROM 99.9% Al_2O_3
+ AFTER O_2 ANNEAL

TABLE I

Initially the temperature was reduced in steps of 10 °C by manually shifting the set point. Although this gave good quality crystal platelets, on later runs the temperature was programmed and controlled using a personal computer. The voltage from a Pt6%Rh-Pt30%Rh thermocouple mounted close to the crucible was read by the computer via a digital microvoltmeter at 10 second intervals. The furnace was switched on and off by the computer depending on the sign of the measured temperature deviation (or on alternate cycles its time derivative). Near 970 °C the thermocouple temperature typically oscillated by ± 2 °C over a period of 3 minutes. Temperature variations of the more massive crucible may well have been much smaller.

As noted in table I difficulties due to the molten mixture reacting with crucible and creeping up the walls have occurred. These were reduced by evaporating gold on the inside of the bucket shaped crucibles and in one case a 12 μm gold layer was deposited electrochemically. Because of material constraints we do not break crucibles to search for crystals. Instead they are cleaned with hot "acqua regia" and used again. On most runs the crucible was tipped on to its side at 950 °C so that the flux flowed away from the crystals. Synthesis in flowing oxygen rather than air did not give any clear improvement.

Shiny black platelets typically 1x2x.05 mm^3 were obtained several times, but the superconducting transition temperature (Tc) remained rather low even after annealing in flowing oxygen gas at 450-500 °C for up to ten days. For the crucibles which had to be coated with gold to avoid loss of flux the maximum onset temperature obtained was 75K.

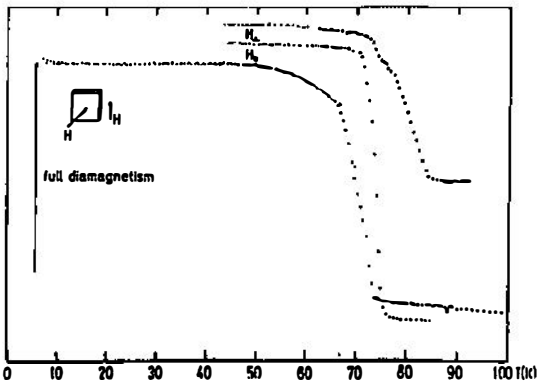

Figure 2

AC susceptibility data for such a crystal are shown in Figure 2. Recently using a different type of alumina crucible /3/ thin platelets were obtained with Tc = 81 K (Figure 2), but even after O_2 annealing these have a broad transition for H_{AC} parallel to the ab plane.

We believe that in many cases we have been unable to oxygenate the crystals fully. Raman measurements /4/ on crystals whose Tc remained at 60 K, even after ten days O_2 annealing, showed that the oxygen content x was well below 7 and X-ray diffraction measurements (by O. M.) showed an almost tetragonal structure. Grinding some of these crystals into powder and oxygen annealing (10 days at 460 °C) increased Tc from 60 to 75 K.

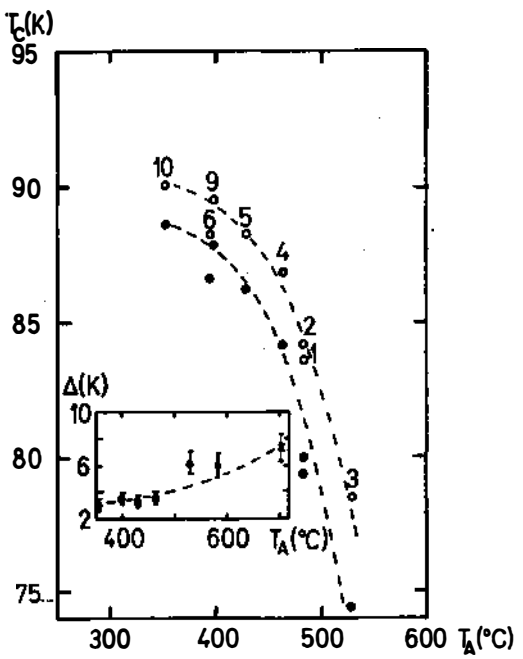

Figure 3

In contrast, using the same equipment, some thicker crystals prepared by G. Collin /5/ can be oxygenated much more easily. A systematic oxygen annealing study of two crystals has been made and some results are shown in Figure 3. The oxygen was initially removed by heating in air to 680 °C, holding for 30 minutes and cooling to room temperature in about the same time Tc was thereby lowered

to below 50 K. Then the 0.5x0.5x0.1 mm^3 crystal was annealed in flowing oxygen for successive 12 hr. periods (numbered in Fig. 3) at various temperatures (T_A). After each anneal the crystal was furnace cooled in 4 hrs to room temperature and Tc was measured using the AC susceptibility technique. The curve of Tc vs. T_A is shown in Figure 3. The open circles represent the 10% transition point in χ_{AC} and the full circles the maximum in $d\chi_{AC}/dT$. From these results it is clear that a twelve hour O_2 anneal is sufficient at 480 ^oC for the above size crystal. For T_A=400 ^oC Tc is improved by 4 K but then longer time scales are required. The uniformity of oxygen concentration was later checked by grinding the crystals down to half their thickness and remeasuring χ_{AC}. The results in Figure 3 are slightly surprising because earlier work /6/ showed that the equilibrium value of x is 6.9 at 530 ^oC in one atmosphere of O_2 and many investigators have shown that Tc is insensitive to x near x=7, but our results definitely show that 530 ^oC is too high a temperature for annealing. In these crystals the transition width for H in the ab plane was narrow, the FWHM in $d\chi/dT$ (Δ in Figure 3) being as low as 3 K. In contrast many of thin plate-like crystals that we have measured (prepared here and in other groups) show a very broad transition in the AC susceptibility for H in the ab plane /2/ (although often not for $H \perp ab$). Furthermore there are often sharp steps or shoulders in $\chi_{AC}(T)$.

Recently a related superconductor $Y_2Ba_4Cu_7O_{14+x}$ has been discovered /7/ in which pairs of CuO2 planes are separated alternately by single Cu chains (typical of the 123 structure) and double Cu chains (typical of the $YBa_2Cu_4O_8$ compound). The steps observed in χ_{AC} could indeed be due to sub-phases with intermediate stacking sequences as proposed in /7/. Since the new compound has only a weakly orthorombic structure (a/b = 1.005 compared to 1.017 in $YBa_2Cu_3O_7$) the presence of extra Cu chains could impede the orthorhombic distortion of the 123 regions and prevent oxygen uptake. In order to check this possibility some platelet crystals were examined by one of us (G. B.) using energy dispersive X-ray analysis and compared with an Orsay crystal (Figure 3) taken to be 1:2:3 stoichiometry. The Tc = 60K crystals (Table I) had Y:Ba:Cu ratios of 1:2.1-2.4:3.1-3.5, depending on the crystals and the particular area studied. A Tc = 75K crystal had ratios of 1:1.8-2.0:2.6-3.5 again the spread in values corresponds to five different areas. In the above measurements no aluminium or gold contamination was detected down to 0.5 and 0.2 wt% respectively. It is interesting to note that in $Y_2Ba_4Cu_7O_{14}$ some Ba substitution for Y occurs /7/. Thus in conclusion we believe that the crystals we have produced until now may well contain some extra copper chains which hinder the orthorhombic distortion and prevent the uptake of oxygen at least on the time scales found to be adequate for the crystals in Figure 3. AC susceptibility measurements for H parallel to the ab plane provide a good way of checking the quality of these crystals.

We acknowledge helpful discussions with E. Babić, G. Collin, A. Hamzić, F. Mattacotta, M. Miljak, D. Mihailović, M. Prester and M. Nevriva..

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