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COMPOSITIONALLY DEPENDENT SUPERCONDUCTING TRANSITION TEMPERATURE OF Y-Ba-Cu OXIDES

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The superconducting transition temperatures of a family of Y-Ba-Cu oxides have been explored by dc resistivity measurements. Substitutions of magnetic and non-magnetic ions on Y, Ba and Cu sites are reported. For some compositions, achieving high superconducting transition temperatures is strongly dependent on growth conditions for the material.

The important discovery of superconductivity above 30 K in La-Cu-O by Bednorz and Müller [1] has led to unprecedented research activity in the field of superconducting oxides and high temperature superconductivity. Wu et al. [2] recently reported superconductivity above 90 K in a mixed phase material $Y_{1.2}Ba_{0.8}CuO_y$; similar findings were made independently but subsequently by Bourne et al. [3]. Structural analyses by other groups [4] suggest that the phase responsible for the superconductivity in these Y-Ba-Cu-O compounds is $YBa_2Cu_3O_{6.9}$.

We have explored the composition dependence of the superconducting transition temperature T_c in a series of Y-Ba-Cu-O compounds, with substitutions made on the Y, Ba and Cu sites. Both magnetic and non-magnetic substitutions are reported. In the pure Y-Ba-Cu-O compound, enhancements of T_c on the order of 7 K are achieved by changes in Y-Ba-Cu-O stoichiometry. Some compositions of Y-Ba-Cu-O are particularly prone to unusual high temperature resistive fluctuations.

Polycrystalline samples were prepared by mixing appropriate starting materials (oxides, carbonates) in a ball mill. In some cases the mixture was then pressed into a small pellet at 5000 psi and then sintered under flowing oxygen between 950–1000°C. In several cases better samples (as distinguished by sharper and higher resistive transitions) were obtained by first sintering the mixed powder at 950°C under flowing oxygen, regrinding the powder, and then pressing the pellets for final firing. Roughly rectangular bars cut from the pellets were used for dc electrical resistivity measurements using a four terminal configuration with silver paint contacts. Typical contact resistances were on the order of a few ohms; typical sample resistances at room temperature were on the order of 0.1 Ω. The samples were cooled in a helium gas flow cryostat.

Fig. 1a shows a typical resistance (R) versus temperature (T) plot for a $YBa_2Cu_3O_y$ sample. The room temperature resistivity is approximately $\rho = 1.76 \times 10^{-2}$ Ω cm. Between 300 and 100 K, R decreases smoothly with decreasing T, but it does not extrapolate to zero at $T=0$. Near $T=125$ K, there is a change in the curvature of R versus T, and at $T_{co}=92$ K, R begins to fall dramatically. We identify T_{co} with the onset of superconductivity in the specimen. The transition width is very narrow, on the order of 2 K. At $T_{cf}=90$ K the resistance has dropped to zero. The midpoint of the transition, which we define as T_c, is at 91 K.

Fig. 1b shows similar resistance data for an $YBa_4Cu_5O_y$ specimen. The data indicate $T_{co}=102$ K, $T_c=98$ K, and $T_{cf}=97$ K. The "1–4–5" (Y:Ba:Cu) stoichiometry was consistently found to have a higher superconducting transition temperature than the "1–2–3" compound, if both materials were first sintered in powder form and then reground. The $T_c=98$ K for the "1–4–5" material represents the highest

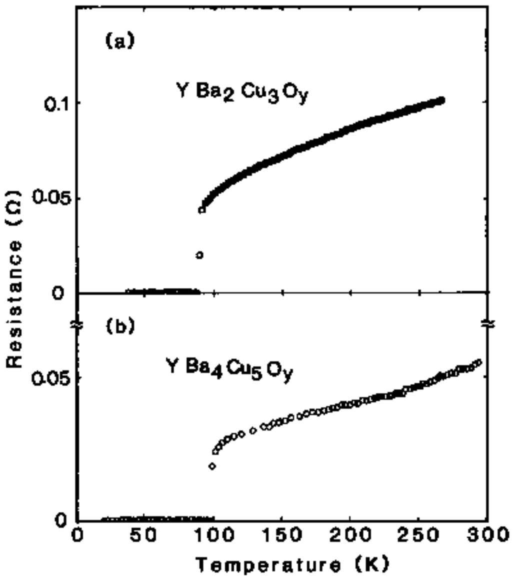

Fig. 1. (a) Resistance versus temperature for $YBa_2Cu_3O_y$. (b) Resistance versus temperature for $YBa_4Cu_5O_y$.

reproducible midpoint superconducting transition temperature that we have obtained.

In the Y–Ba–Cu–O compound, Y sites are separated by Ba site layers. In the "1–2–3" compound, the Y sites are separated by two Ba sites, measured along the c axis. In the Y–Ba–Cu–O "1–4–5" compound, 50% of the Y sites have been substituted with Ba, hence one expects for this material four Ba sites between successive Y sites. At present we do not have detailed structural information on our samples to confirm this assumption.

We have made additional substitutions on the Y and also the Ba and Cu sites. Table 1 summarizes our results for successful superconducting transitions. It is noteworthy that up to 2% doping of the Cu ion by magnetic Co does not destroy the superconductivity, although T_c is significantly lowered. It is also interesting that 100% substitution of magnetic Gd on the Y sites has virtually no effect on T_c [5]. We have not been successful in achieving superconducting behavior by fully replacing the Y by Sc, or the Ba by Pb or Rb.

We have also investigated the possibility that T_c in the Y–Ba–Cu oxides can be significantly increased by annealing the materials in oxygen under moderate pressure. Annealing an Y–Ba–Cu–O "1–2–3" compound in 3 atm O_2 at 700°C for several hours changed the material from a metal to an insulator at room temperature (following the high pressure anneal, the predominant sample phase had changed from black to green in color). Annealing in 3 atm O_2 at 500°C for several hours had no appreciable effect on T_{co}, but the transition became more smeared. In some samples, the superconducting transition in the treated samples was preceded by semiconducting (increasing R with decreasing T), rather than metallic, behavior for T above T_{co}.

In many samples of Y–Ba–Cu–O, we have observed unusual drops in resistance with decreasing temperature, at temperatures well above 100 K, often as high as 230–240 K [3]. $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$ seems particularly prone to such anomalies. Fig. 2 shows the most dramatic anomaly we have observed. Fig.

Table 1
Characteristic superconducting onset (T_{co}), midpoint (T_c), and final $R=0$ (T_{cf}) critical temperatures for Y–Ba–Cu oxides.

Material	T_{co} (K)	T_c (K)	T_{cf} (K)
$YBa_2Cu_3O_y$	92	91	90
$YBa_3Cu_4O_y$	98	96	92
$YBa_4Cu_5O_y$	102	98	97
$Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$	92	91	90
$Y_{0.025}Sc_{0.025}Ba_{0.45}Cu_{0.5}O_y$	80	77	74
$Y_{0.5}Sc_{0.5}Ba_2Cu_3O_y$	90	65	38
$YBa_2Cu_{2.985}Co_{0.015}O_y$	90	88	85
$YBa_2Cu_{2.97}Co_{0.03}O_y$	75	65	60
$YBa_2Cu_{2.94}Co_{0.06}O_y$	75	72	67
$YBa_2Cu_{2.4}Au_{0.6}O_y$	84	78	72
$YBa_2Cu_3Mg_xO_y$	64	53	41

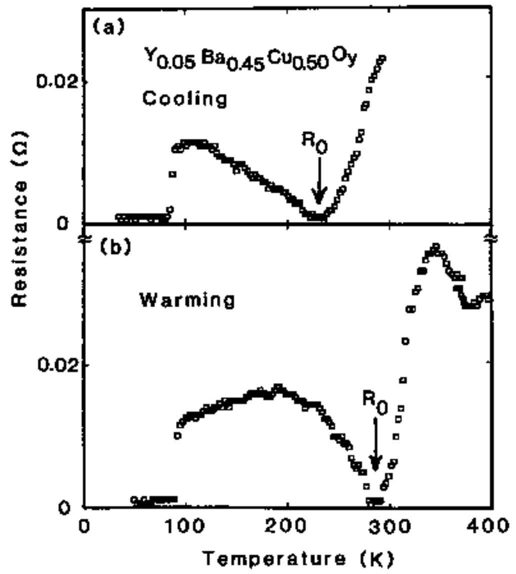

Fig. 2. (a) Resistance versus temperature upon cooling for a particular $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$ sample. (b) Same as (a), but for warming. The strong anomalies in R above 90 K are not obtained after temperature cycling the sample. The vertical arrows identify the R_0 state described in the text, where $R_0 < 10^{-4}$ Ω.

2a shows R versus T for an $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$ sample cooled from room temperature. A well-defined minimum resistance R_0 state (identified by a vertical arrow) is apparent at 230 K, where, within the experimental resolution of 10^{-4} Ω, R is zero. Decreasing T further results in an upturn and subsequent turnover in R. At $T_c = 91$ K, a conventional superconducting transition is observed. Fig. 2b shows R versus T for the same $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$ sample upon warming. T_c is again 91 K, but the high temperature minimum in R is shifted to above 275 K. Between 280 and 292 K, the R_0 state was again observed. The state was stable and was destroyed only upon heating the specimen to above room temperature. Subsequent cooling of the same specimen did not result in a zero resistance state above 91 K. Our polycrystalline samples are not necessarily homogeneous and one might assume the presence of multiple phases in the $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$ specimen. It is not unreasonable to tentatively identify the R_0 state near 230 K in fig. 2a and near 290 K in fig. 2b with a superconducting filament running the length of the sample, where the filament is easily broken by temperature cycling of the sample. However, our experimental resolution of 10^{-4} Ω does not allow superconductivity to be distinguished from good metallic conductivity.

Resistive anomalies above 100 K in the Y–Ba–Cu–O compounds are somewhat tenuous at present, and we cannot generate them at will. We also emphasize that we have not been able to duplicate the high temperature R_0 state described in fig. 2. However, the possibility of unusual phases in $Y_{0.05}Ba_{0.45}Cu_{0.5}O_y$, where there are presumably nine Ba sites between successive Y sites, is intriguing, and deserves further study.

In summary, the superconducting transition temperature of the Y–Ba–Cu–O system has been explored and is found to be sensitive to substitutions on the Y, Ba, and Cu sites. The highest reproducible T_c we have observed is 98 K, in $YBa_4Cu_5O_y$.

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