Phase diagram and superconductivity in the Y-Ba-Cu-O system

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We have determined the phase diagram of the Y-Ba-Cu-O system through structural, superconducting critical temperature and critical current density characterization. Our results show that a single-phase compound with a stoichiometry $YBa_2Cu_3O_y$ is responsible for the high-temperature superconductivity (92.5 K) in this system.

The discovery of high-temperature superconductivity in perovskite-related oxides has generated an enormous amount of activity. Superconductivity above 30 K was initially reported by Bednorz and Müller[1] in a multiphase system having a nominal stoichiometry of $La_{5-x}Ba_xCu_5O_{5(3-y)}$. Subsequent to this, Takagi et al.[2] identified the superconducting compound as $(La_{1-x}Ba_x)_2CuO_4$ with the K_2NiF_4-type structure. Substitution of Ba by Sr was shown to produce relatively narrow superconducting transitions with zero resistance near 40 K.[3-6] Recently, Wu et al. reported for the first time superconductivity above 90 K in a multiphase sample having the nominal composition of $Y_{1.2}Ba_{0.8}CuO_{4-\partial}$,[7] and suggested that multiphase samples are necessary for the occurrence of such high critical temperatures.

Contrary to this suggestion, we believe that the superconducting behavior exhibited by the material $Y_{1.2}Ba_{0.8}CuO_{4-\partial}$ is in fact caused by a single minority phase in their multiphase sample. In this letter we report an extensive study of the part of the Y-Ba-Cu-O phase diagram in which superconductivity appears. From this diagram, determined using x ray and neutron diffraction coupled with transport measurements, we conclude that the superconducting material is a single phase.

A large number of samples of various compositions were prepared by standard powder metallurgical methods starting with 99.999% pure Y_2O_3, $BaCO_3$, and CuO powders. After thorough mixing, grinding, and pressing, the samples were sintered at approximately 1000 °C in flowing O_2 for 6 h, then slowly furnace cooled. X-ray powder diffraction patterns were obtained using a SCINTAG PAD V computerized theta-theta diffractometer. Neutron diffraction patterns of possible stoichiometric compounds in the system were obtained at the Argonne National Laboratory Intense Pulsed Neutron Source (ANL-IPNS) on the Special Environment Powder Diffractometer (SEPD). Transport measurements, using 0.1–1 A/cm² in the 8.5–320 K range, were made using a computer-controlled closed-cycle refrigerator capable of measuring five samples simultaneously. Temperatures were measured using SiO diode thermometry traceable to NBS standards and are accurate to about 0.5 K over the measured temperature range. Critical current density measurements were made in boiling liquid nitrogen (77 K) on cut bars approximately 1 mm²×10 mm long. The critical currents are defined using a 1-μV/cm voltage criterion.

The Y-Ba-Cu-O phase diagram is shown in Fig. 1. The initial atomic percent of the metals in the starting composition is used to determine the position of each sample on the phase diagram. This phase diagram is a projection of the quaternary phase diagram onto the zero-oxygen plane, with nominal oxygen content *inferred* by *assuming charge balance*. Several single-phase stoichiometric compounds have been identified by comparison to known x-ray diffraction patterns. These compounds (indicated by a ▨ in Fig. 1) form the boundaries of the mixed phase regions outlined in the diagram. Although the BaO-rich region of the phase diagram has not been fully investigated, we have evidence of an unidentified compound in this area below the 45% Cu concentration line. Thus no phase line exists joining the green Y_2BaCuO_5 with the $BaCuO_2$ compound. The triangular phase regions appearing in our diagram are, in reality, pro-
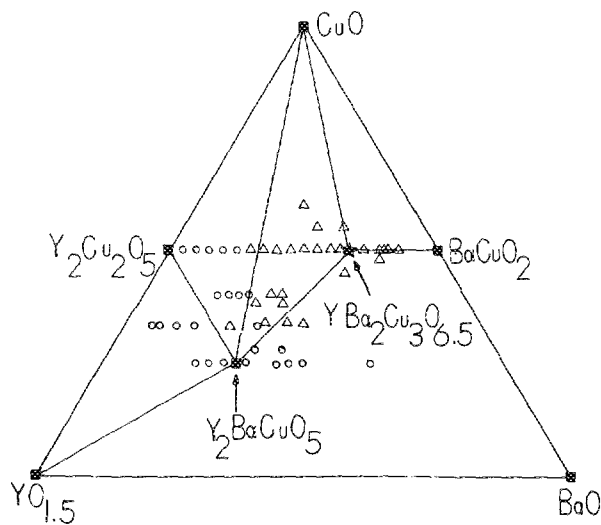

FIG. 1. Projection of the quaternary Y-Ba-Cu-O phase diagram onto the zero-oxygen plane. The nonmetallic and superconducting phases are indicated by open circles and triangles, respectively. The stoichiometric compounds are indicated by closed squares and the $YBa_2Cu_3O_{6.5}$ superconducting compound is marked as a star.

jections of four-cornered polyhedra; consequently the number of phases in equilibrium could exceed the number depicted in the figure. However, this has not been observed, suggesting that the major features of the phase diagram are relatively insensitive to atomic percent oxygen. The possible dependence on oxygen concentration and/or dependence on the preparation conditions is under investigation. The symbols on the phase diagram denote only those samples which have been fully characterized by x ray, resistivity, and critical current measurements. It can be seen that only those samples in phase regions containing $YBa_2Cu_3O_{6.5}$ are superconducting near 90 K. No superconductivity is observed (down to 8.5 K) in samples residing outside these regions. This indicates that $YBa_2Cu_3O_{6.5}$ is the high T_c superconducting compound in this system.

Both neutron (Fig. 2) and x-ray diffraction patterns demonstrate that $YBa_2Cu_3O_{6.5}$ exists as a single-phase material. As one moves away from $YBa_2Cu_3O_{6.5}$ along the $(Y_{1-x}Ba_x)Cu$ composition line (50% Cu), in either direction from the stoichiometric compound, new peaks appear in the diffraction pattern. For $x < 0.67$ peaks attributable to Y_2BaCuO_5 and CuO appear, while for samples with $x > 0.67$, only $BaCuO_2$ is observed, consistent with the two-phase line shown in Fig. 1. From this we conclude that there exists a single-phase compound with the stoichiometry $YBa_2Cu_3O_{6.5}$. *We should stress that the oxygen concentration is inferred from charge balance considerations and that we*

FIG. 3. (a) Onset of the superconducting transition temperature (T_c^{onset}) and the zero resistance temperature (T_c^0) vs increasing Ba composition (x) along the $(Y_{1-x}Ba_x)Cu$ composition line; (b) critical current density at 77 K vs increasing Ba composition $(\times)$.

have not verified this by independent measurements. In addition, as one moves away from the single-phase $YBa_2Cu_3O_{6.5}$ towards the $BaCuO_2$ compound, along the 50% Cu line, the orthorhombic splitting decreases. This may be due to small stoichiometry changes in the oxygen or metal ion sublattices.

Evidence that this compound is the superconducting phase is obtained from both resistivity and critical current measurements. In Fig. 3(a) we plot the onset temperature (T_c^{onset}) of the superconducting transition and the zero resistance temperature (T_c^0) versus x along the $(Y_{1-x}Ba_x)Cu$ composition line. T_c^{onset} is essentially constant with varying Ba concentration (x), demonstrating that a single phase with a well defined stoichiometry is responsible for the superconductivity. This is in contrast to the $La_{1-x}Sr_xCuO_4$ system where large variations in T_c over a small composition range are observed.[8] As a more sensitive probe of the fraction of superconducting material in each sample, the critical current density J_c was measured at 77 K. The critical current density versus composition is plotted in Fig. 3b. Note that J_c exhibits a maximum (168 A/cm^2) at $x = 0.67$ $(YBa_2Cu_3O_{6.5})$, indicating that the volume fraction of superconductor is largest at this composition.

Samples with a higher barium content $(x > 0.67)$ had a higher porosity than those with $x < 0.67$. This would account for the rapid decrease in J_c to very low values (< 2 A/cm^2) for $x > 0.67$ which in turn is in accordance with the reduction in T_c^0 for these samples as illustrated in Fig. 3(a). The higher porosity sets a lower limit for the J_c because the cross section of the sample used in the J_c calculation is incor-
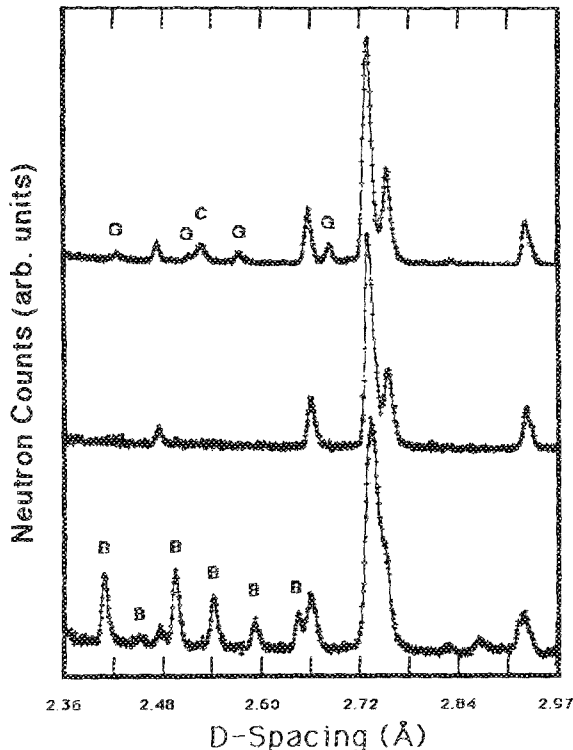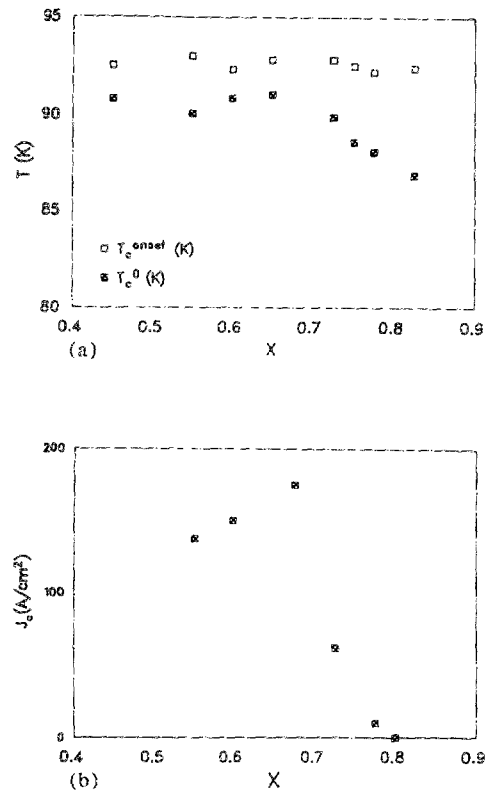

FIG. 2. Neutron diffraction patterns which show the appearance of secondary phases as the stoichiometry moves away from $YBa_2Cu_3O_{6.5}$: upper curve for $Y_2Ba_1Cu_5$ nominal metal ion composition, middle curve for the stoichiometric superconductor $YBa_2Cu_3O_{6.5}$, and lower curve for the YBa_4Cu_5 nominal metal ion composition. The impurity phases are identified according to the following symbols: $B = BaCuO_2$, $G =$ green Y_2BaCuO_5, and $C = CuO$.

rect and may also cause a reduction in pinning strength due to differences in sample morphology.

In this letter we clearly demonstrate, through a combination of structural and transport measurements on many samples, the existence of a single stoichiometric compound, $YBa_2Cu_3O_{6.5}$, which is responsible for superconductivity in the Y-Ba-Cu-O system. The relatively small number of quaternary compounds observed in the phase diagram implies that samples which contain a fraction of this compound can be prepared over a wide composition range. Starting from the Y-rich side, increasing the Ba composition will result in the sudden appearance at the phase boundary of superconductivity and the associated x ray and neutron peaks of the $YBa_2Cu_3O_{6.5}$ compound. Such an observation could be misinterpreted as the identification of a superconducting phase with a composition consistent with the starting formula. Although the critical currents measured are rather low compared to the 10^4 A/cm^2 necessary for typical superconducting applications, we note that these J_c's are 100 times greater than those previously observed in $La_{1-x}Sr_xCuO_4$.[3] In addition, since no effort has been made to enhance the J_c of these materials either through densification of the pellets or optimization of pinning structures, a current density of 168 A/cm^2 at 77 K in these materials presents the distinct possibility of superconducting applications at liquid nitrogen temperatures.

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