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Reexamination of the Y_2O_3-BaO-CuO phase diagram for solid solutions near $Y_1Ba_2Cu_3O_7$

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In a previous communication the results of critical-temperature and Hall-effect measurements on compounds off the stoichiometric $Y_1Ba_2Cu_3O_{7-x}$ composition were interpreted as an indication that a narrow range of solid solutions exists for the superconducting compound. Present data show that the earlier results were due to oxygen deficiency in the off-stoichiometry samples and that no evidence exists for solid solutions off or on the 50%-Cu line between $Y_2Cu_2O_5$–$BaCuO_2$ of the ternary Y_2O_3–BaO–CuO phase diagram.

Of all the new oxide superconductors in which the existence of bulk superconductivity has been unambiguously confirmed, the generic compound $Y_1Ba_2Cu_3O_{7-x}$ (1:2:3), which crystallizes in a perovskite-related structure, has exhibited the highest critical temperature T_c, which is between 90 and 100 K. This compound is formed with a stoichiometric composition in the ternary Y_2O_3-BaO-CuO whose schematic phase diagram is shown in Fig. 1. The existence of solid solutions for small deviations from the 1:2:3 stoichiometry would make it possible to observe a systematic dependence of superconducting and normal-state properties upon the composition. This, in turn, could contribute to the understanding of transport and superconductivity mechanisms in this new class of materials. Hinks *et al.*,[1] however, investigated the ternary phase diagram by x-ray diffraction (XRD), neutron diffraction, and resistivity versus temperature measurements, and observed no indication of the formation of a solid solution in their samples. However, we reported[2] that magnetic-susceptibility, resistivity, and Hall-effect data in samples of (A) $Y_{1.05}Ba_{1.8}Cu_{3.0}O_{7-x}$ and (B) $Y_{1.0}Ba_{2.2}Cu_{3.0}O_{7-x}$ composition indicated the existence of a narrow range of solid solutions for compositions off the 50%-Cu line between $Y_2Cu_2O_5$–$BaCuO_2$.

In this Brief Report we present the results of additional studies on compositions A and B which indicate that our original interpretation was incorrect and that the observed properties arose from an oxygen-deficient 1:2:3 phase rather than from a solid solution. In addition, we prepared and characterized six off-stoichiometry compositions located on the 50% Cu line. For these compositions, as well, we find no evidence that a solid solution was obtained.

Methods of sample preparation and characterization were as described before.[2] An additional, final step in the preparation procedure following the reaction at 940 °C was to anneal the sample at 400 to 450 °C for 16 h in oxygen to ensure an oxygen content close to seven atoms per formula unit and a complete transformation from tetragonal to orthorhombic structure. The original samples of the off-50% Cu compositions were given this additional anneal as were the freshly prepared ones.

A detailed examination of XRD diffractometer traces was made for each sample with reference to now available standards of several secondary phases and the tetragonal 1:2:3. In both original and reproduced off-50% Cu samples, small amounts of $Y_2Ba_1Cu_1O_5$ (2:1:1), Ba_2CuO_3, and $BaCuO_2$ second phases were present. Prior to additional annealing the original samples also contained the tetragonal 1:2:3 phase. Upon annealing, the tetragonal phase disappeared or its presence was greatly reduced. The intensity of (2:1:1) lines decreased in composition (B) and increased in (A). Table I compares the properties of the off-50% Cu compositions, as previously reported, with those obtained after additional annealing. The original and freshly prepared annealed samples gave the same results. It is seen that both T_c from susceptibility and n^* increased upon annealing to values typical of the 1:2:3 composition. Also, the content of the superconducting phase increased. Table II includes analogous data for on-line compositions. Again, no compositional dependence of T_c or n^* was found. All off-stoichiometry samples, even at the smallest deviation from stoichiometry, contained minor amounts of secondary phases.

The results presented above make it clear that the lower values of T_c (from susceptibility) and n^* originally re-

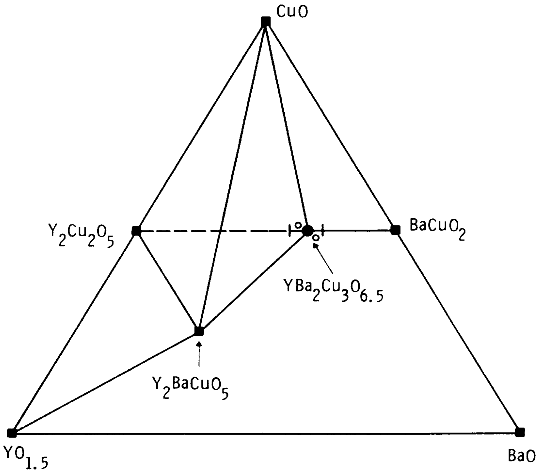

FIG. 1. Schematic phase diagram for ternary system Y_2O_3-BaO-CuO. The open circles indicate the off-50% Cu compositions (A) and (B) discussed in the text, and the vertical bars indicate the range of compositions studied on the 50% Cu line.

TABLE I. Effect of oxygen annealing (1:2:3 compound was annealed at 700 °C for 36 h; others were annealed at 400 °C for 16 h) at 400 °C on T_c and superconducting volume fraction in powder and effective carrier density in sintered pellets.

Composition cations only	T_c (K) Onset from χ Original	Annealed	Superconducting volume (%) Original	Annealed	n^* (cm^{-3}) Original	Annealed
$Y_{1.0}Ba_{2.0}Cu_{3.0}$	87	91	⋯	100	1.4×10^{21}	4.2×10^{21}
$Y_{1.5}Ba_{1.8}Cu_{3.0}$	70	89	90	100	9.4×10^{20}	4.7×10^{21}
$Y_{1.0}Ba_{2.2}Cu_{3.0}$	70	88	55	86	8.3×10^{20}	3.2×10^{21}

TABLE II. Effect of deviation from the 1:2:3 stoichiometry along the 50% Cu line between $Y_2Cu_2O_5$ and $BaCuO_2$.

Composition cations only	T_c (K) Onset from susceptibility	ρ_{148} ($\mu\Omega$ cm)	n^* (cm^{-3})
$Y_{0.80}Ba_{2.20}Cu_3$	91	2.8×10^3	4.2×10^{21}
$Y_{0.90}Ba_{2.10}Cu_3$	91	920	7.2×10^{21}
$Y_{0.95}Ba_{2.05}Cu_3$	91	660	5.3×10^{21}
$Y_1Ba_2Cu_3$	91	390	7.6×10^{21}
$Y_{1.05}Ba_{1.95}Cu_3$	91	530	6.0×10^{21}
$Y_{1.10}Ba_{1.90}Cu_3$	92	620	6.1×10^{21}
$Y_{1.20}Ba_{1.80}Cu_3$	92	620	7.0×10^{21}

ported for off-stoichiometry samples and interpreted as an indication of compositional dependences over a range of solid solutions were, in fact, due to oxygen deficiency in the stoichiometric 1:2:3 major phase. Criticality of conditions required for obtaining the maximum possible oxygen content was not yet fully recognized in the first weeks following the discovery of the 1:2:3 phase. We have found no evidence of the formation of 1:2:3 solid solutions in the ternary diagram.

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