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Superconductivity above Liquid Nitrogen Temperature: Preparation and Properties of a Family of Perovskite-Based Superconductors

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Over the last decade, the search for high-temperature superconducting materials remained virtually stagnant. This situation changed radically with the discovery of Bednorz and Müller¹ of superconductivity above 30 K in a layered perovskite oxide composed of La, Ba, and Cu. Improvements in the superconducting transition temperature (T_c) to ~45 K by Sr substitution and identification of the phase responsible for superconductivity ($\text{La}_{2-x}\text{Ba}(\text{or Sr})_x\text{CuO}_y$, where x is typically between 0.1–0.3)^{2–6} followed rapidly. The next major advance was immediate and dramatic. Wu, Chu, and co-workers reported⁷ a new material based on the starting composition $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_y$, with T_c well above 90 K. Nearly simultaneous reports by other groups^{8,9} confirmed these results. The Y–Ba–Cu material was a mixture of several unidentified phases and only a small fraction of the sample actually was superconducting. Recently, the structure of this new superconductor was identified as an oxygen-defect perovskite corresponding to the composition $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y$.^{10–12}

In this paper, we report on the synthesis of single-phase $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y$, and show how the preparation conditions play a dramatic role in determining the superconducting properties. Also,

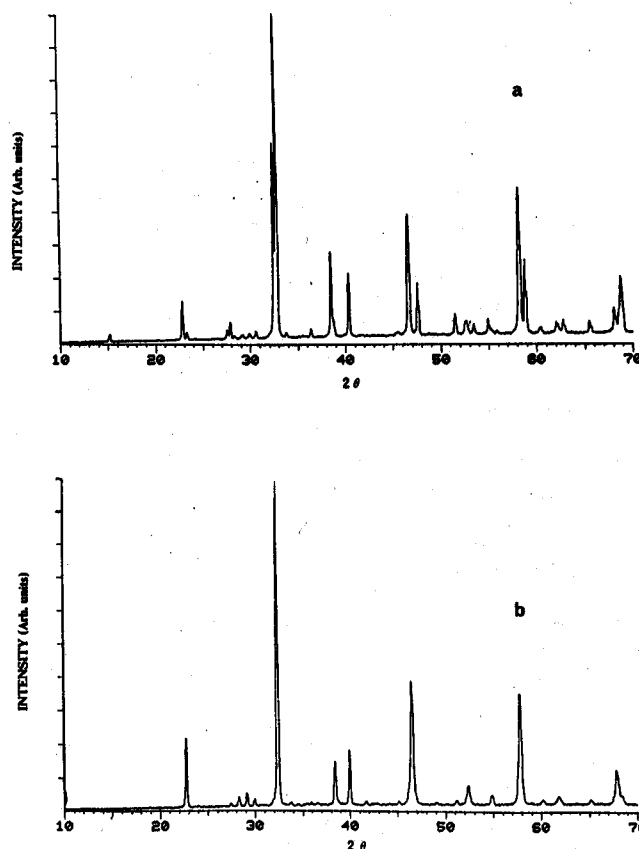


Figure 1. X-ray powder diffraction patterns for (a) $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y$, and (b) $\text{Pr}_1\text{Ba}_2\text{Cu}_3\text{O}_y$.

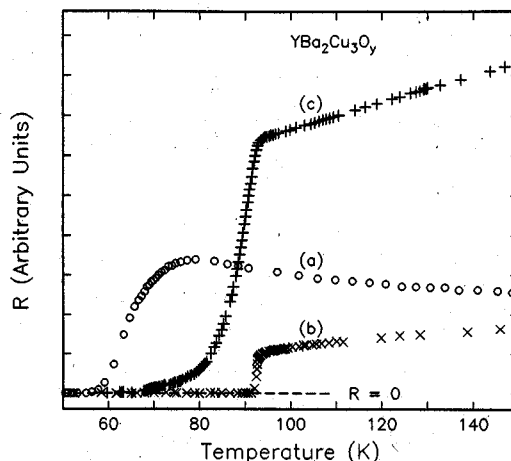


Figure 2. Plot of four-probe electrical resistivity vs. temperature for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y$, under various preparative conditions: (a) fast removal of pellets from oxygen anneal at 900 °C; (b) slow cooling of oxygen annealed sample from 900 to 200 °C over 5 h; (c) same as (b) except air anneal.

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Table I. Superconducting Properties of $Y_1Ba_2Cu_3O_y$ Derivatives

compd	T onset	T_c (midpoint), K	ΔT_c (90–10% value), K
$YBa_2Cu_3O_y$	98	94	2
$NdBa_2Cu_3O_y$	80	~45	~50
$SmBa_2Cu_3O_y$	90	85	8
$EuBa_2Cu_3O_y$	98	92	1
$GdBa_2Cu_3O_y$	92	86	8
$DyBa_2Cu_3O_y$	95	91	2
$HoBa_2Cu_3O_y$	96	92	1
$YbBa_2Cu_3O_y$	93	90	2
$LuBa_2Cu_3O_y$	45	32	~20
$Y_{0.5}Sc_{0.5}Ba_2Cu_3O_y$	94	90	4
$Y_{0.5}La_{0.5}Ba_2Cu_3O_y$	90	80	10
$Y_{0.5}Lu_{0.5}Ba_2Cu_3O_y$	96	92	1
$YSrCaCu_3O_y$	85	82	3
$YBaSrCu_3O_y$	89	85	1
$YBaCaCu_3O_y$	87	82	1
$YbBaSrCu_3O_y$	85	81	2
$YbBaCaCu_3O_y$	85	81	2

based on our knowledge of the structure, we have prepared a variety of new, single-phase high-temperature superconducting compounds in which Y and Ba are substituted by related elements, demonstrating that 90+ K superconductivity is a more general property of this structure.

The synthesis of these new superconductors followed standard methods previously described for perovskite oxides.¹³ This involved intimately mixing the oxide or carbonate powders and calcining at temperatures ranging from 900 to 1100 °C. For the $Y_1Ba_2Cu_3O_y$ materials, we found the following procedure gave the best results. Ultrapure Y_2O_3 , $BaCO_3$, and CuO were mixed in a ball mill or a mortar and pestle in a 1:2:3 ratio of Y, Ba, Cu. The powder was heated in an alumina boat at 950 °C under flowing oxygen for 12 h. The resulting black powder was reground and heated again under similar conditions. At this stage, X-ray diffraction confirmed complete reaction to the desired phase (Figure 1a). For measurement purposes, the powder was usually cold-pressed (1500 psi) into pellets and sintered at 700–900 °C for several hours under oxygen flow. The most critical step in achieving high-temperature superconductivity and sharp transitions was the rate of quenching from the oven. Figure 2 illustrates this sensitivity for similarly prepared pellets of $Y_1Ba_2Cu_3O_y$. When rapidly removed to room temperature, a broad phase transition centered around 60 K was obtained (curve a). Slow cooling over 5–6 h to room temperature raised T_c above 90 K with transition widths (10–90% value) of a couple of degrees (curve b). The superconducting properties were also sensitive to the oxygen partial pressure in the annealing ambient. Heating in air (curve c) lowered and broadened T_c compared to heating in pure oxygen; however, the oxygen pressure effect was minor in comparison to the quench rate effect.

The sensitivity to quench rate is likely due to changes in the oxygen content and ordering in these oxygen-defect structures. Michel and Raveau¹⁴ have previously shown in related structures that variation in the oxygen content can convert the defect perovskite from a semiconductor to a metal. Electron microprobe analysis on polished pellets of $Y_1Ba_2Cu_3O_y$ determined the oxygen content to be 7.4 ± 0.3 .¹⁵ Oxygen can be reversibly removed by annealing in argon, which gives an insulating material.

The structure of the high-temperature superconducting phase is reported in detail elsewhere.^{16,17} It is basically a pseudotet-

ragonal (orthorhombic), distorted perovskite, with yttrium and barium ions in separate layers between square-planar Cu–O sheets. This gives rise to a layered-like structure, somewhat analogous to $La_{2-x}Ba_xCuO_y$ (which adopts the K_2NiF_4 structure).³

In contrast to $La_{2-x}Ba_xCuO_y$, where doping with other rare-earth elements suppresses superconductivity,¹⁸ we have found that both Y and Ba can be replaced with little effect on the superconducting properties. Table I summarizes the properties of the various derivatives of $Y_1Ba_2Cu_3O_y$ that we have prepared using the procedure described above. Some general observations emerge. The larger rare earth ions did not show superconducting behavior (La, Ce, Pr). Nd begins a broad resistivity change at 80 K which continues to 10 K before reaching zero. From Sm to Yb, fairly sharp transitions are obtained with T_c ¹⁹ around 90 K. Lu gives an anomalously low transition. Presently, it is not clear whether the poorer superconducting behavior of Lu and Nd, and its absence in La, Ce, and Pr, are artifacts of the preparation procedure. X-ray powder diffraction on Lu, Nd, and Pr derivatives confirm them as single-phase materials with the desired structure. However, the orthorhombic distortion (i.e., $a \neq c$) as evidenced by the splitting of particular diffraction peaks is reduced, as illustrated in Figure 1b for $Pr_1Ba_2Cu_3O_y$. The lattice parameters for this material are $a = 3.845$, $b = 11.801$, and $c = 3.905$ Å, where as for $Y_1Ba_2Cu_3O_y$ they are $a = 3.820$, $b = 11.688$, and $c = 3.894$ Å. The possible relationship of this small structural distortion to superconductivity is currently under investigation. Ce and La derivatives do not appear to have formed the desired structure and are certainly multiphase. Attempts to replace Y with other trivalent ions such as Sc and Tl have been unsuccessful; however, combinations such as $Y_{0.5}Sc_{0.5}$, $Y_{0.5}La_{0.5}$, and $Y_{0.5}Lu_{0.5}$ all produced high T_c materials. X-ray diffraction indicates the major phase is that of the superconducting structure; however, minor phases are also present. Replacement of Ba with either Sr or Ca did not yield superconductors after repeated attempts. Surprisingly, substitution of Sr_1Ca_1 for Ba_2 did give a superconducting compound with a $T_c \sim 85$ K, as did Ba_1Sr_1 and Ba_1Ca_1 . The fact that the magnetic rare earth ions (e.g.: Gd, Dy, Sm, etc.) do not significantly affect superconductivity is consistent with structural analysis^{16,17} and band structure calculations.^{20,21} The rare-earth and alkaline-earth ions appear to be only weakly coupled to the two-dimensional network of Cu–O sheets over which both normal and superconducting transport occurs. We have also examined the sensitivity of T_c to slight off-stoichiometry variations of Y and Ba. All variations of the type $Y_{1\pm 0.2}Ba_{2\pm 0.2}Cu_3O_y$ displayed sharp transitions ($\Delta T = 1\text{--}2$ K) centered around 92 K. The extent to which these off-stoichiometry compositions are accommodated by the perovskite-based structure without the formation of additional phases is currently under investigation.

In summary, we have prepared a wide variety of new high-temperature superconducting compounds, demonstrating that the discovery of superconductivity above liquid nitrogen temperature is not limited to one quaternary system. Further, such variations are likely to be useful in probing subtle details of the relationship of structure to superconducting properties. Moreover, such a range of materials will clearly be valuable for the myriad of applications that are sure to follow.

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