Superconductivity at 90 K in the Tl-Ba-Cu-O System

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Stable and reproducible superconductivity has been unambiguously observed in a new Tl-Ba-Cu-O system containing no group-III*B* elements. Resistance in these rare-earth–free oxides starts to drop sharply above 90 K and reaches zero at 81 K. Meissner flux expulsion and diamagnetic shielding show bulk superconductivity. Further substitutions of elements for this system may lead to even higher-temperature superconductors.

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The high-temperature superconducting La-Ba-Cu-O system discovered by Bednorz and Müller[1] has a special feature; that is, the elements in this system can be replaced partially or completely by other elements, producing even higher-temperature superconductors. Substitution of Sr for Ba has produced 40-K superconductivity.[2,3] Substitution of Y for La has produced different crystal structure with an increased transition temperature of 90 K.[4] The compound responsible for the high-temperature superconductivity in the latter case was rapidly identified as $YBa_2Cu_3O_{7-x}$ with perovskite structure.[5] A large class of 90-K superconducting compounds of the form $RBa_2Cu_3O_{7-x}$ with R=La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm Yb, and Lu were prepared by further substitutions of other rare earths (Y is considered in the rare-earth category in this Letter) for Y in $YBa_2Cu_3O_{7-x}$.[6,7] Later, 90-K superconductivity in the radioactive Th-Ba-Pb(Zr)-Cu-O system was reported.[8] Recently, an unstable 50-K superconductor, $YBa_2Ag_3O_{7-x}$, was also reported.[9] To date, three of the elements belonging respectively to groups III*B*, II*A*, and I*B* are required for all high-temperature oxide superconductors (the only exception is 40-K superconductivity of La_2CuO_4),[10,11] and only partial substitutions of other elements have led to superconductivity, but with no significant increase in transition temperature.

In this Letter, we report a new Tl-Ba-Cu-O superconducting system which contains no rare-earth elements. Resistance measurements show that this superconducting system has an onset temperature above 90 K with a zero resistance ($<10^{-6}$ Ω cm in resistivity) at 81 K. Magnetic measurements confirm the superconducting transition. The samples are stable in air at ambient temperature for at least two months (according to resistance-temperature remeasurements) and their preparation is easily reproduced. We believe that the discovery of this new superconductive system will provide deeper insight into mechanism of high-temperature superconductivity and may lead to even higher-temperature superconductors by variations of composition and preparation procedures, and/or by further elemental substitutions.

Samples were prepared from 99.999%-pure Tl_2O_3, 99.999%-pure $BaCO_3$, and certificate reagent CuO. A typical procedure for the preparation of Tl-Ba-Cu-O samples, in which some principles of the melt process which we developed for preparing high-quality melt-processible $RBa_2Cu_3O_{7-x}$ superconductors[12,13] are used, is as follows: Appropriate amounts of $BaCO_3$ and CuO were mixed and ground with an agate mortar and pestle, and heated in air at 925 °C for more than 24 h with several intermediate grindings to obtain a uniform black Ba-Cu-oxide powder (for example, $BaCu_3O_4$ or $Ba_2Cu_3O_5$). Appropriate amounts of Tl_2O_3 and Ba-Cu-oxide powder with a certain nominal composition (for example, $TlBaCu_3O_{5.5+x}$ and $Tl_{1.5}Ba_2Cu_3O_{7.3+x}$, hereafter denoted by 1-13 and 1.5-23, respectively), were completely mixed and ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1–2 mm. A quartz boat containing the pellet was then put into a tube furnace, which had been heated to 880–910 °C, and was heated for 2–5 min in flowing oxygen. As soon as it had slightly melted, the sample was taken out from the furnace and quenched in air to room temperature. The samples are black, porous, and multiphase. It must be emphasized that slight melting of the samples is crucial to a sharp superconducting transition above liquid-nitrogen temperature.

Electron-probe microanalysis showed considerable composition disparity between points in the samples studied, which can be a result of either actual differences

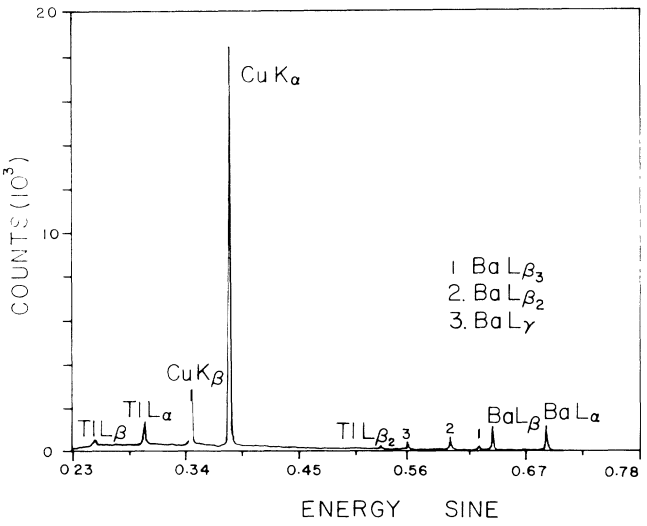

FIG. 1. Wavelength-dispersive spectroscopy scan (LiF detector) of a superconducting sample of $TlBaCu_3O_{5.5+x}$.

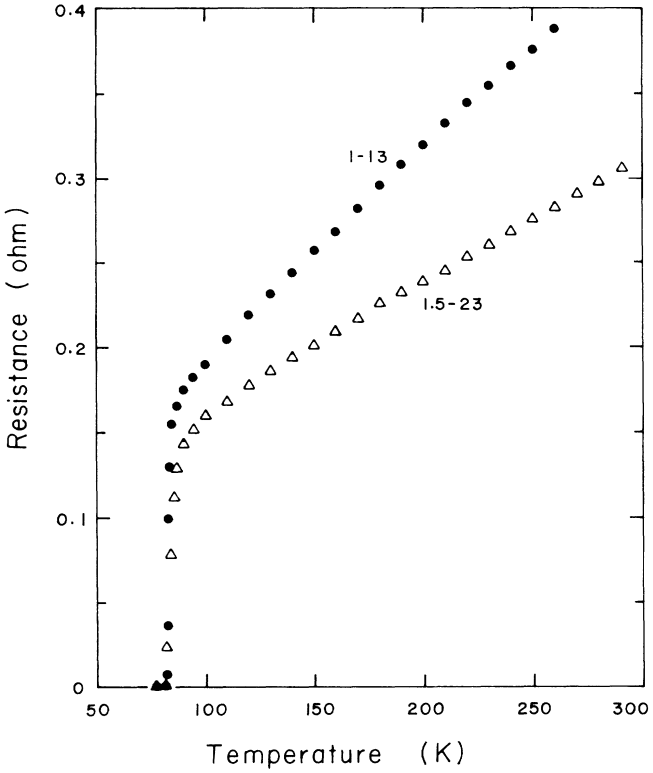

FIG. 2. Variations of resistance with temperature for samples of $TlBaCu_3O_{5.5+x}$ (1-13) and $Tl_{1.5}Ba_2Cu_3O_{7.3+x}$ (1.5-23).

in composition or surface topography or both. In general, average compositions of the samples are close to their nominal (starting) compositions. Care was taken to search thoroughly for peaks from rare-earth elements with the use of wavelength-dispersive spectroscopy scans of a 1-13 sample with a Cameca model MBX electron-probe microanalyzer. All peaks in the spectra taken either with a LiF detector or with a PET detector can be assigned to Tl, Ba, or Cu. No unambiguous peaks from rare-earth elements were seen in the spectra, and we conclude that rare-earth elements, if present, would be in concentration less than 0.1 at.%, too small an amount to account for the superconducting behavior observed. Figure 1 shows the wavelength-dispersive spectroscopy scan for the 1-13 sample taken with a LiF detector.

Resistance was measured by the standard four-probe technique with silver-paste contacts. Rectangular bars of typical size $7\times3\times1$ mm^3 were cut from the pellets for resistance measurements. Figure 2 shows the variations of resistance with temperature for samples 1-13 and 1.5-23 (all 1-13 samples used in the present experiments were prepared in the same batch). The variations of resistance with temperature of the Tl-Ba-Cu-O samples are similar to those observed for typical $RBa_2Cu_3O_{7-x}$ samples: The resistance decreases nearly linearly with decreasing temperature to just above the superconducting onset temperature, and then sharply drops. The ratio of resistance at room temperature to that at onset temperature is above 2. Both samples have onset temperatures of above 90 K and midpoints of about 84 K, and reach zero resistance at 81 K. The width of the resistance transition (10% to 90% points) is 2–3 K. Average resistivity of the samples is about 10 mΩ cm at room temperature if we assume a porosity of 20%. The actual resistivity of the current-carrying phase will certainly be much less than this value since the samples are multiphase.

Magnetization measurements were made on a BTI variable-temperature SQUID susceptometer. The susceptibility for the sample 1-13 is shown in Fig. 3 (the sample weight was 0.1022 g). The circle points were obtained when the sample was cooled to 5 K in zero field, and then a field of 2 mT was applied and the sample was warmed (these data represent flux exclusion or diamagnetic shielding). The triangle points were obtained when the sample was cooled in the same field (Meissner expulsion) and represent the volume fraction of perfect superconducting response. The diamagnetism-onset temperature was about 85 K, slightly lower than the onset of resistance drop, similar to other high-temperature oxide superconductors.[14] Meissner expulsion at 10 K was 15% of diamagnetic shielding and represented about 5% of perfect superconductivity. The zero-field cooling data (circles) do not display the saturation behavior we normally observe in $RBa_2Cu_3O_{7-x}$ samples.[15] The behavior in Fig. 3 resembles that of La_2CuO_{4-y}:Ba, which Müller, Takashige, and Bednorz[16] describe as superconductive glass behavior, and that of nonstoichiometric Y-Ba-Cu-O samples.[17,18]

In order to identify the phase(s) responsible for superconductivity in the Tl-Ba-Cu-O samples, we carried out secondary-electron imaging and powder x-ray diffrac-

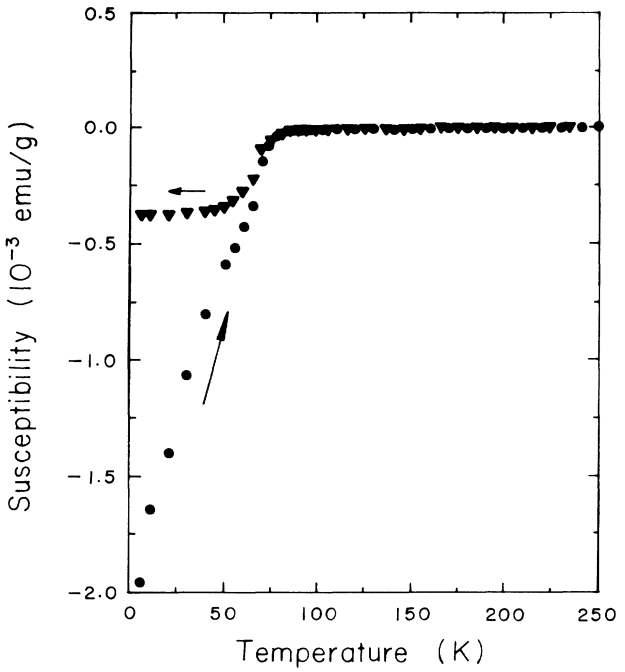

FIG. 3. Susceptibility vs temperature for a 1-13 sample. As indicated with arrows, the circles were obtained during warming in a field of 2 mT after cooling in zero field, and the triangles were obtained during cooling in the same field.

tion. Secondary-electron imagings were performed with a JEOL model 840 scanning electron microscope with an Oxford liquid-helium cold stage on the 1-13 sample in the superconducting state at 75 K and in the normal state at 110 K. We failed to see an unambiguous change of secondary-electron yield below and above the transition temperature,[19] possibly because of the small volume fraction of the superconducting material at 75 K (see Fig. 3). Powder x-ray diffraction was carried out with Cu $K\alpha$ radiation with use of a DIANO DTM 1057 diffractometer. Figures 4(b)–4(d) show powder x-ray diffraction patterns for three 2-23 samples, A, B, and C. Sample A was simply a mixture of Tl_2O_3 and $Ba_2Cu_3O_5$. Sample B was the same, but heated at 775 °C for 5 min, and had an onset temperature just above 77 K. Sample C was heated at 900 °C for 4 min and reached zero resistance at 81 K (note that the stoichiometry of this sample is different from those of Fig. 2). Figure 4(a) shows the diffraction pattern for a $Ba_2Cu_3O_5$ sample and Fig. 4(e) for an $YBa_2Cu_3O_{7-x}$ sample, for comparison. It can be seen that the heated superconducting samples B and C, compared with the unheated sample A, have two additional peaks: one at just below a 2θ of 33° and another at about 57°. The former is a characteristic of the $RBA_2Cu_3O_{7-x}$ perovskite as shown in Fig. 5(e) (also see, for example, Ref. 5). At present, we cannot say if these peaks originate from a new type of superconducting crystal structure. Detailed phase identification and

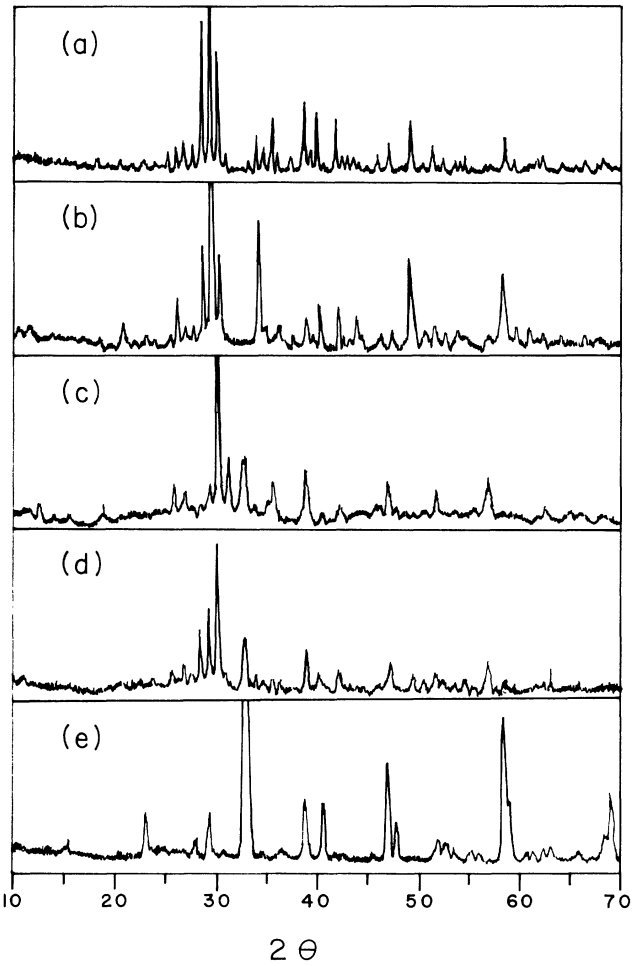

FIG. 4. Powder x-ray diffraction patterns. (a) $Ba_2Cu_3O_5$; (b) $Tl_2O_3+Ba_2Cu_3O_5$; (c) $Tl_2Ba_2Cu_3O_{8+x}$, heated at 775 °C; (d) $Tl_2Ba_2Cu_3O_{8+x}$, heated at 900 °C; and (e) $YBa_2Cu_3O_{7-x}$.

structure analysis are in progress.

The discovery of the new superconductive Tl-Ba-Cu-O system above liquid-nitrogen temperature dispels the myth that elements in the rare-earth category are required for high-temperature superconductivity. Detailed discussion of this new superconducting system must await complete composition and structure analysis, but we would like to point out here that (a) rare earths have valence-electron configuration $6s^24f^n5d^{0/1}$ (Y has $5s^24d^1$), whereas thallium has $6s^26p^1$; (b) rare-earth oxides are insulators, whereas Tl_2O_3 has a low resistivity of 10^{-4} Ω cm at room temperature[20] and is metallic above liquid-nitrogen temperature,[21] and itself may be superconducting.[22] Therefore, one might expect that a thallium-containing system would have many interesting transport properties not seen in rare-earth-containing systems.[21] We believe that the new superconducting Tl-Ba-Cu-O system will provide deeper insight into the understanding of the mechanism of high-temperature oxide

superconductivity, and may lead to higher-temperature superconductors.

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