

Bulk Superconductivity at 125 K in $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$

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Bulk superconductivity is reported in $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$ with a transition to zero resistance at ≈ 125 K, the highest transition temperature (T_c) yet found. Transmission electron spectroscopy shows that the unit cell is body-centered tetragonal and contains trilayer Cu perovskitelike units separated by bilayer Tl-O units. T_c in this material varies from 118 to 125 K depending on preparation conditions. A high density of perovskitelike bilayer intergrowths are observed in the 118-K material, which we speculate result in the decreased T_c . A second structure containing only bilayer perovskitelike units— $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_x$ —is a bulk superconductor with T_c ranging from 95 to 108 K.

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Following the recent discovery of high-temperature superconductivity in the Bi-Sr-Ca-Cu oxide system,¹⁻⁹ Hermann *et al.*¹⁰ have reported superconducting transitions in a Tl-Ca-Ba-Cu oxide composite with onset temperatures of up to 120 K and with zero resistance below ≈ 107 K. Two superconducting phases, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_{8+\delta}$, were identified in their samples by Hazen *et al.*¹¹ In this Letter we report the observation of bulk superconductivity with a transition to zero resistance at 125 K in $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$, the highest superconducting transition temperature yet found. We find that the superconducting transition temperature can be varied from 125 to 118 K for the same nominal structure and composition depending on processing conditions.

Samples were prepared by our thoroughly mixing appropriate quantities of Tl_2O_3 , CaO, BaO, and CuO. After grinding, the mixture was pressed into a pellet, wrapped in gold, and fired at 880°C for approximately 3 h in a sealed quartz tube containing ≈ 1 atm of oxygen. A wide variety of starting compositions was studied, producing multiphase material in all cases whose component compositions bore little relation to the starting material. Electron microprobe analysis¹² found the multiphase materials to be comprised of significant amounts of two quinary oxides of Tl-Ca-Ba-Cu-O. Analysis carried out on a large number of grains of these phases revealed metal cation stoichiometries of approximately $\text{Tl}_{1.64}\text{Ca}_{1.87}\text{Ba}_2\text{Cu}_{3.11}$ and $\text{Tl}_{1.70}\text{Ca}_{1.06}\text{Ba}_2\text{Cu}_{2.32}$, which we will henceforth refer to as 2223 and 2122, respectively. Other major phases included a quaternary oxide containing the cations Tl, Ca, and Cu in approximate proportion Tl:Ca:Cu:O = 0.04:0.41:0.55, as well as oxides of Ca and Ba depending on the starting composition. These various phases were interwoven with one another, but extended networks of the quinary oxides were formed with crystallites up to 50 μ in size. The surface of the pellets was found in many cases to be almost completely depleted of the Tl-Ca-Ba-Cu oxide phases and to be comprised of the quaternary $\text{Tl}_{0.04}\text{Ca}_{0.41}\text{Cu}_{0.55}$ oxide for up to several

hundred microns, giving rise to problems with the formation of electrical contacts. Our starting with an overall composition corresponding to one of the quinary oxides did not result in large amounts of that phase, in agreement with the results of Hazen *et al.*¹¹ We found that starting metal cation compositions of $\text{Tl}_1\text{Ca}_3\text{Ba}_1\text{Cu}_3$ and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3$ gave rise to the largest percentages of the 2223 and 2122 phases, respectively. The magnetic, transport, and structural properties of these materials were reproducible for repeated preparations and stable over the course of these experiments.

A curve of resistance versus temperature for a sample of starting composition $\text{Tl}_1\text{Ca}_3\text{Ba}_1\text{Cu}_3\text{O}_x$ is shown in Fig. 1. The resistance drops to zero at 125 K within the experimental limit of 10^{-8} Ω . The measurements were carried out with a standard low-frequency lock-in method with four probes and platinum paint contacts. The temperature dependence of the Meissner susceptibility, measured with an S.H.E. Corp. (B.T.I.) dc SQUID

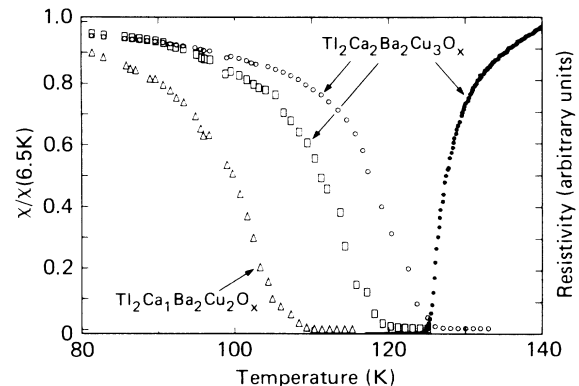


FIG. 1. Resistance vs temperature (filled circles) for a material of starting composition $\text{Tl}_1\text{Ca}_3\text{Ba}_1\text{Cu}_3\text{O}_x$. Meissner susceptibility (normalized to 1 at 6.5 K) vs temperature for materials with starting composition $\text{Tl}_1\text{Ca}_3\text{Ba}_1\text{Cu}_3\text{O}_x$ (open circles), $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$ (rectangles), and $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_x$ (triangles) for an applied field of 100 Oe.

magnetometer, for the same sample is also shown in Fig. 1. It displays an abrupt transition whose temperature is in excellent agreement with that determined from the transport data. The diamagnetic shielding signal for this sample at low temperatures was approximately twice as large as the Meissner signal for a measuring field of 100 Oe and was $\approx 20\%$ of $-1/4\pi$. Larger fractions were found at smaller fields.

The variation of the relative amounts of Ca and Ba in the starting material away from 3:1 gave rise to material with transition temperatures close to 118 K. Meissner data for a typical pellet of starting composition $Tl_1Ca_2Ba_2Cu_3$ are shown in Fig. 1. A study of a number of samples of starting composition $Tl_1Ca_xBa_1Cu_3$, where x was varied from 3 to 2, showed that the superconducting transition temperature could take intermediate values between 118 and 125 K, while the magnitude of the Meissner signal was little changed. Meissner data are also included in Fig. 1 for a sample containing virtually no 2223 material but large amounts of the 2122 phase. This material, prepared from a starting composition of $Tl_2Ca_2Ba_2Cu_3$, had a transition temperature of ≈ 108 K and the Meissner fraction was approximately 12%. However, other samples containing predominantly the

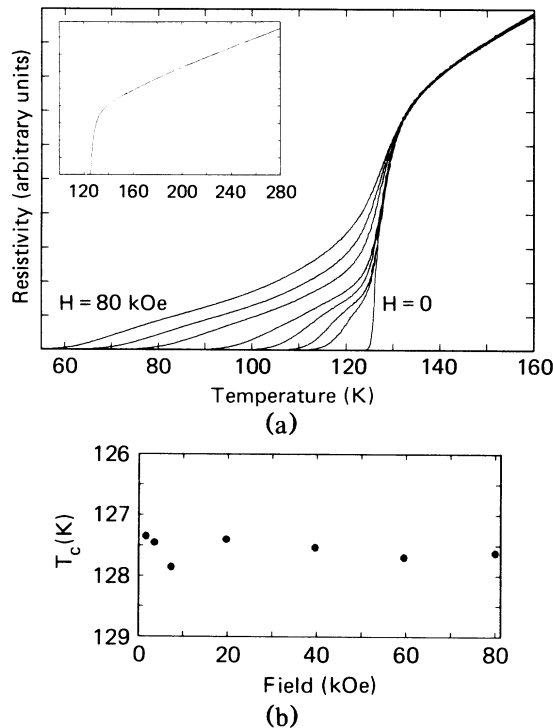


FIG. 2. (a) Resistance vs temperature for a sample of starting composition $Tl_1Ca_3Ba_1Cu_3O_x$ for magnetic fields of 0, 0.81, 1.62, 3.54, 7.3, 19.7, 19.7, and 80.0 kOe, applied transverse to the current direction through the sample. Inset: $H = 0$ resistance curve to higher temperatures. (b) Magnetic field vs transition temperature obtained from the data in (a) as described in the text.

2122 phase had transition temperatures ranging from 108 to 95 K.

Measurements of the critical fields were made on a $Tl_1Ca_3Ba_1Cu_3O_x$ sample. Values of H_{c1} of a few hundred oersteds were found from magnetization studies at 6.5 K. The resistive transition was found to be very sensitive to small fields, with a significant lowering of the zero-resistance temperature even for fields of ≈ 100 Oe, as shown in Fig. 2(a). This result is not surprising given that the sample contains perhaps only $\approx 50\%$ of the superconducting phase and these crystallites may be weakly coupled together. However, consistent with the substantial Meissner susceptibility and large superconducting crystallites in these materials, Fig. 2(a) shows that there remains a well-defined transition at high magnetic fields even though superimposed on an extended "foot." Numerical differentiation of the resistance curves with use of a sliding quadratic least-squares fit gave a narrow, well-defined peak at the inflection point seen in the curves of resistance versus temperature [Fig. 2(a)], which we used as a reasonable definition of the transition temperature. The transition temperatures determined in this way are shown in Fig. 2(b) versus applied field. Within the experimental error of ± 0.5 K, no change in transition temperature is found for fields of up to 8 T, indicating a very high upper critical field.

The microstructures of the $Tl_1Ca_3Ba_1Cu_3$, $Tl_1Ca_2Ba_2Cu_3$, and $Tl_2Ca_2Ba_2Cu_3$ samples were examined by electron microprobe analysis, x-ray powder diffractometry, and transmission electron microscopy (TEM). Both microprobe analysis and x-ray powder diffractometry indicated that the $Tl_1Ca_3Ba_1Cu_3$ sample contained significant amounts of the 2223 phase, but virtually no 2122 phase. By comparison of the diffraction pattern from this sample (Fig. 3) with those from samples with similar starting compositions, it was possible to extract those reflections that correspond to the 2223 phase. These reflections could be indexed to a tetragonal cell with dimensions $3.822(4) \times 3.822(4) \times 36.26(3)$ Å³. Electron

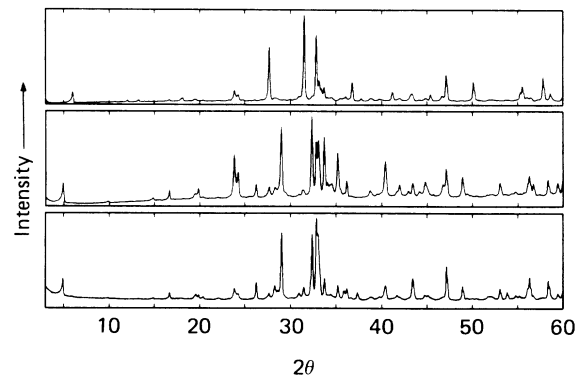


FIG. 3. X-ray powder spectra (Cu radiation) for powdered pellets of starting composition $Tl_2Ca_2Ba_2Cu_3O_x$ (upper), $Tl_1Ca_2Ba_2Cu_3O_x$ (middle), and $Tl_1Ca_3Ba_1Cu_3O_x$ (lower).

diffraction studies found the crystals to be body-centered tetragonal with space group $I4/mmm$ at room temperature. High-resolution TEM images along the [100] direction in these crystals [Fig. 4(a)] revealed that the structure consists of trilayer copper perovskitelike units separated by bilayer Tl-O units. If the image can be treated as a projected charge density of the crystal, then the Tl and Ba columns should be much darker than the Ca and Cu columns. Thus, we interpret the alternating bands of light and dark contrast as evidence for a -Tl-Ba-Cu-Ca-Cu-Ca-Cu-Ba-Tl- stacking sequence. Minor amounts of a third quinary oxide that was face-centered orthorhombic and twinned were also found in this sample.

For the $Tl_1Ca_2Ba_2Cu_3$ sample, there was a slightly greater amount of the 2122 phase than in the 1313 material. X-ray diffraction indicated that the unit cell of the 2223 phase in this sample was tetragonal with dimensions $3.821(2) \times 3.821(2) \times 36.23(2) \text{ \AA}^3$. Both high-resolution images and electron-diffraction patterns showed that most of the 2223 crystals in this sample contained stacking faults along the c axis that correspond to bilayer perovskite intergrowths. Apparently these inter-

growths and the accompanying changes in composition result in a reduced transition temperature in this sample.

The $Tl_2Ca_2Ba_2Cu_3$ sample produced the largest fraction of 2122 crystals, but no 2223 crystals. The x-ray diffraction peaks from the 2122 phase were easily distinguished from the 2223 phase. The unit cell derived from the x-ray data was tetragonal with $a = 3.857(1) \text{ \AA}$ and $c = 29.39(1) \text{ \AA}$. Electron-diffraction studies also found these crystals to be body-centered tetragonal with space group $I4/mmm$ at room temperature. High-resolution images along the [100] direction [Fig. 4(b)] revealed that the 2122 structure consists of bilayer copper perovskitelike units separated by bilayer Tl-O units. Once again we interpret the image contrast as evidence for a -Tl-Ba-Cu-Ca-Cu-Ba-Tl- stacking sequence.

Finally, we note that selected-area electron-diffraction patterns from both the 2223 and 2122 phases showed evidence for additional ordering. Further details of our structural studies will be published shortly.

In summary, we have found bulk superconductivity at 125 K in one member of a new class of high-temperature superconductors. This material, $Tl_2Ca_2Ba_2Cu_3O_x$, has a structure comprised of trilayer Cu perovskitelike slabs separated by bilayer Tl-O units. A closely related compound, $Tl_2Ca_1Ba_2Cu_3O_x$, whose structure contains bilayer copper perovskitelike slabs, superconducts at 108 K. Further determination of the relationship between the various structural types in this family and the way in which subtle modifications to them affect superconductivity may lead to improved understanding of this phenomenon.

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Note added.— We have recently prepared a new family of compounds of the form $Tl_1Ca_nBa_2Cu_{n+1}O_x$ ($n=1,2,3$) in which the Cu perovskitelike units are separated by monolayer Tl-O units.¹³ As for the materials described in this Letter, the superconducting transition temperature increases with increasing number of Cu-O planes, although the transition temperatures are a little lower for each compound. Since both the size and separation of the Cu perovskitelike units can be independently varied, the Tl-Ca-Ba-Cu-O system provides an ideal family of structures with which to test various models of high-temperature superconductivity.

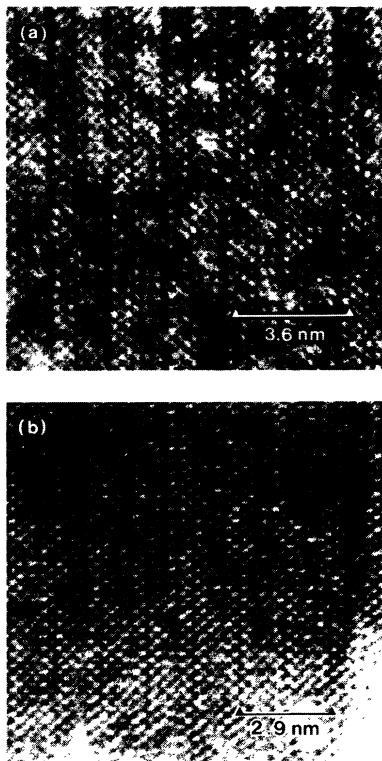


FIG. 4. High-resolution transmission electron micrographs along the [100] zone axes for crystallites of nominal composition (a) $Tl_2Ca_2Ba_2Cu_3O_x$ in a composite of starting composition $Tl_2Ca_3Ba_1Cu_3O_x$ and (b) $Tl_2Ca_1Ba_2Cu_2O_x$ in a composite of starting composition $Tl_2Ca_2Ba_2Cu_3O_x$.

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¹²Electron microprobe analysis was carried out with Cameca model SX50 electron microprobe at a 15-keV accelerating voltage and a 35-nA beam current with an analyzing area of $\approx 1 \mu\text{m}^2$. Atomic concentrations were determined to $\pm 10\%$ relative.

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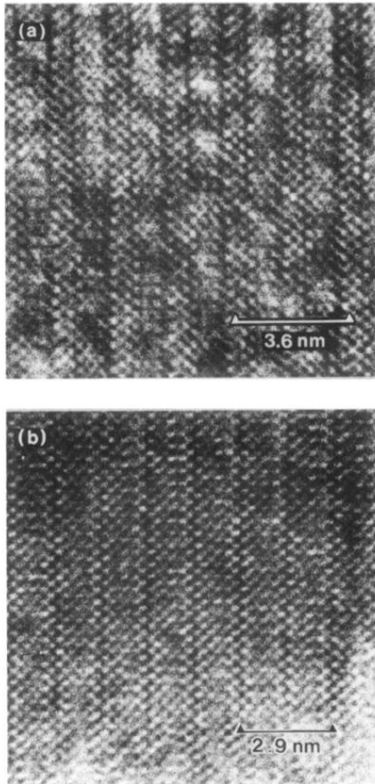


FIG. 4. High-resolution transmission electron micrographs along the [100] zone axes for crystallites of nominal composition (a) $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$ in a composite of starting composition $\text{Tl}_2\text{Ca}_3\text{Ba}_1\text{Cu}_3\text{O}_x$ and (b) $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_x$ in a composite of starting composition $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$.