Anisotropic Seebeck coefficient in Tl$_2$Ba$_2$CuO$_6$ single crystals

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Abstract

Anisotropic Seebeck coefficients have been carefully measured in Tl$_2$Ba$_2$CuO$_6$ single crystals with differing oxygen doping levels. In-plane Seebeck coefficients are small in magnitude ($\sim 5 \mu V/K$), negative at room temperature and have a decreasing magnitude as the temperature decreases. C-axis Seebeck coefficients are larger in magnitude ($\sim 20 \mu V/K$) and positive. The absolute magnitude of the Seebeck coefficients (all directions) increases as the oxygen (hole) doping levels increase in these overdoped materials. In samples with high transition temperatures, a crossover from negative to positive occurs $\sim 15 K$ above the superconducting transition temperature. The good correlation between bulk compound data and appropriately weighted in-plane and c-axis crystal data is shown. The data are discussed in terms of single-band and multiband models but none are uniquely identified as appropriate for these complex materials.

1. Introduction

Since its discovery [1], Tl$_2$Ba$_2$CuO$_6$ (Tl-2201) has been one of the most interesting high-temperature superconductor systems available for study. It is one of the simplest HTSC crystal structures containing only one Cu–O plane per formula unit [2]. The superconducting transition temperature, $T_c$, of this system can be tuned over a large temperature range (0 to 92 K) by simple oxygen or inert gas (N$_2$, He, Ar) annealing [3] (oxygen acts as a p-dopant). In this paper we present and discuss measurements of the anisotropic Seebeck effect of Tl-2201 single crystals as a function of $T_c$ (hole doping).

The first Seebeck measurements on Tl-2201 were reported by Dyadakin et al. [4]. They show data for one bulk ceramic sample with $T_c < 40 K$. Weeks et al. [5] reported measurements on bulk samples with $T_c$'s of 80 and 60 K. These were supplemented by measurements on Ce doped Tl-2201 compounds [6]. Obertelli et al. measured Seebeck data on bulk samples of Tl-2201 with $T_c$'s ranging from 0 to $\sim 80 K$ [7]. Zhang et al. reported anisotropic data on one crystal with $T_c \sim 80 K$ as grown in our lab [8]. We now report anisotropic measurements on crystals of varying $T_c$ from the same growth batch as that reported in Ref. [8].

2. Experimental

The crystals were grown using a self-flux method [9] and were selected for lack of growth steps on the surface, lack of intergrowth lines, thinness, and sharp edges. Dimensions were approximately 1 mm $\times$ 0.5
Flux-creep activation energies in Tl₂Ba₂CaCu₂Oₓ single crystals

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The measured frequency shift in temperature of the ac susceptibility Tl₂Ba₂CaCu₂Oₓ single crystals is modeled by an Arrhenius-like expression to give flux-creep activation energies at various applied ac magnetic fields ranging from 15 to 200 Oe. The activation energies range from 288±14 meV in an applied ac magnetic field of 15 Oe to 25±3 meV in 200 Oe. Considerable flux creep is observed. It is estimated that $H_c^*$ at a temperature of about 100 K is approximately 10 Oe. The results are interpreted in terms of Anderson flux-creep model and the activation-energy values reported here are similar to those deduced from magnetic-field-dependent resistivity measurements on the TI-based single crystals, textured films, and bulk samples. The field dependence of the activation energies is observed to vary as $1/\sqrt{H}$. This low-field dependence is explained by a scaling argument where the vortex volume is approximated by $\xi^2a_0$, with $\xi$ the coherence length in the $ab$ plane and $a_0$ the Abrikosov vortex-lattice spacing along the $c$ axis of the crystal lattice.

INTRODUCTION

Flux pinning plays a key role in realizing high critical current densities in high temperature superconductors and much attention has been focused on this subject. Palstra et al. measured the resistive transition in a single crystal of Bi$_2$Sr$_2$CaCu$_2$O$_{8-}\delta$ in large dc magnetic fields and showed that flux creep was thermally activated, as defined by the Arrhenius resistivity expression $\rho(T,H) = \rho_0 \exp(-U(H)/kT)$, with magnetic field-dependent pinning energies ranging from 30 to 300 meV near $T_c$. Using the same technique, Sun et al. showed that the activation energies in ErBa$_2$Cu$_3$O$_{7-}\delta$ were much greater when the applied magnetic field was perpendicular to the $c$ axis than when it was parallel.

Yeshurun and Malozemoff used the method of magnetic relaxation, introduced by Kim et al. and Anderson, in single YBa$_2$Cu$_3$O$_{7-}\delta$ crystals to derive the pinning potentials. Ferrari et al. derived a distribution function of the pinning energies for a YBa$_2$Cu$_3$O$_{7-}\delta$ thin film and for a Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$ crystal by measuring the flux noise using a low-noise 4-K SQUID. Nikolov and Goldfarb and Müller, Nikolov, and Driver measured the intergranular activation energies in Y-Ba-Cu-O and (Bi,Pb)-Sr-Ca-Cu-O bulk samples by the method of a frequency shift in ac susceptibility. Here we use this latter method and Anderson's theory of flux creep to find the flux-creep activation energies in Tl₂Ba₂CaCu₂Oₓ (2:2:1:2 phase) single crystals in low ac magnetic fields.

EXPERIMENTAL DETAILS

Volume susceptibility was measured with an ac susceptibilitymeter specifically designed to pick up a small signal from a single crystal. Two sensing coils, connected in opposition to pick up the crystal's signal induced by the primary coil, were used. The sample remained stationary inside one of the sensing coils with the signal from the sample superimposed on the background. Only the real (inductive) part, whose signal is considerably larger than that of the imaginary part, was measured. Several background-only runs were made to confirm the transition. Only samples where the transition was quite distinct were included in the analysis.

To maximize the sensitivity for a single small crystal, the smallest possible dimensions of the sample holder and the sensing coils had to be selected. The smallest temperature diode available is the Lake Shore DT-450 and the sample holder was designed around it. Figure 1 shows the dimensions of the sample holder configuration. The pick-up coils had a 5-mm inner diameter and were wound with a 420-gauge (0.003-in.-diam) wire. A Stanford Research Systems lock-in amplifier, model SR-530 was used to detect the signal from the pick-up coils. The temperature was maintained using an Omega model CYC91 controller with a Nichrome heater wire. The heater coil was oppositely wound to eliminate its magnetic effects. The primary coil was driven with a California Instruments 3213-K high-power constant rms current source.
Anisotropic resistivity and paraconductivity of Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_8$ single crystals

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The anisotropic resistivity and paraconductivity of Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_8$ single crystals were measured. The in-plane and c-axis resistivities are, respectively, $\sim 7 \times 10^{-4}$ and $10^{-1}$ $\Omega$ cm at room temperature. The c-axis resistivity decreases with decreasing temperature in the temperature range from room temperature down to the superconducting transition temperature, and the second derivative of $\rho_c$ is negative, which is not characteristic of YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8$ single crystals, in which the second derivative is either positive or zero. The in-plane paraconductivity is obtained from the in-plane resistivity, and a method without the critical temperature as an adjustable parameter is employed to obtain the dimensionality. The data show that the superconductivity is two dimensional, but a crossover from two to three dimensions has also been observed near the transition temperature in some samples.

INTRODUCTION

Since the discovery of high-temperature superconductivity in the doped copper-oxide systems, there has been much interest in the usual properties of these systems in their normal state. The highly anisotropic electronic structure of the carrier planes and the interaction between the planes are very interesting aspects of the nature of these systems. In the normal state, the resistivity ratio $\rho_c/\rho_p$ (where $\rho_c$ and $\rho_p$ are the resistivities along the c axis and in the a-b planes, respectively) was reported to be as high as $10^2$-$10^4$, and thermal excitation transport in the normal state was observed in the c axis of YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8$ crystals.\(^1\)\(^-3\) The dimensionality of the superconductivity has been discussed in relation to paraconductivity measurements on bulk, thin-film, and single-crystal samples of YBa$_2$Cu$_3$O$_7$ (Refs. 6-8) and Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8$.\(^3\)\(^-5\) In the Tl-Ba-Ca-Cu-O system, measurements were carried out on polycrystalline thin-film and bulk samples.\(^9\)\(^,10\)

In this paper, we report the results of anisotropic resistivity and paraconductivity measurements on single crystals of Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_8$ (2:2:1:2). The $\rho_p$ versus $T$ behavior shows an increase with increasing temperature and is approximately linear above 220 K. Below 220 K, the curve gradually deviates from the linear behavior. In our experiments, $\rho_c$ decreases as the temperature decreases, and the $\rho_p$ versus $T$ curve is not linear, the second derivative is negative. The $\rho_p$-$T$ curve saturates as temperature increases, this may be explained by a resistivity model of a metallic system where the mean free path is close to the Mott limit. We believe the electronic band structure of 2:2:1:2 corresponds to that of a three-dimensional metal with a large anisotropic effective mass. In some crystals, paraconductivity may be fit by a two-dimensional theory in the temperature range from 150 to $\sim 2$ K above transition temperature ($\sim 102$ K), but in other samples, a crossover from two- or three-dimensional behavior occurs at $\sim 5.5$ K above the transition temperature.

EXPERIMENT

Two different processes were used to grow the single crystals. In the first process (A), we used a Ba$_2$Ca$_2$Cu$_3$O$_7$ precursor. Appropriate amounts of BaO, CaO, and CuO (each 99.99% pure) were mixed and ground to form a mixture with a nominal stoichiometry of Ba$_2$Ca$_2$Cu$_3$O$_7$. The mixture was heated in air for 24 h at 920°C, with an intermediate grinding carried out in order to facilitate a complete reaction. The reacted mixture was then ground...
100 K SUPERCONDUCTING PHASE IN THE
TI-Pb-Sr-R-Cu-O SYSTEM WITH R - RARE EARTHS

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Superconductivity around 100 K was observed in the TI-Pb-Sr-R-Cu-O system (R = rare earths) by resistance and ac susceptibility measurements. Powder X-ray diffraction analyses showed that the phase responsible for the superconductivity is of a tetragonal structure with a general formula \((\text{TI}_{1-\delta}\text{Pb}_{\delta})\text{Sr}_{3-\nu}\text{R}_{\nu}\text{Cu}_{2}\text{O}_{7}\) (132 phase).

Discoveries of the 90 K TI-Ba-Cu-O system\(^1,2\) and 120 K TI-Ba-Ca-Cu-O system\(^3,4\) has lead to a number of new TI-based superconducting systems.\(^5-8\) In our own work, we found that the TI-Sr-Ca-R-Cu-O system (R = rare earths) is superconducting around 90 K.\(^7\) Later, we found that the Ca-free TI-Sr-R-Cu-O system was also superconducting at temperatures up to about 90 K.\(^9,10\) Further work showed that when TI was partially substituted by Pb, the TI-Pb-Sr-R-Cu-O system exhibited superconductivity at even higher temperatures around 100 K. In this letter, we report the observation of 100 K superconductivity in the TI-Pb-Sr-R-Cu-O samples and the phase identification based on powder X-ray diffraction data. In the present experiments Pr and Tb were used as the representatives of the light rare earths and the heavy rare earths, respectively. Other rare earths, including Y, also work, and the results will be published in a separate paper.

TI-Pb-Sr-R-Cu-O samples were prepared using high-purity \(\text{TI}_2\text{O}_3\), \(\text{PbO}_2\), \(\text{SrO}\) (SrCO\(_3\), or Sr(NO\(_3\))\(_2\)), \(\text{R}_2\text{O}_3\) (except CeO\(_2\), PrO\(_3\), and TbO\(_3\)), and CuO. In a typical procedure, component compounds with a certain metallic atom ratio were completely mixed and ground. The powder was pressed into a pellet with a diameter of either 7 mm or 15 mm and a thickness of 1–2 mm. The pellet was placed in an alumina boat, and was heated in a preheated tube furnace at 1000–1050°C with flowing oxygen for 2–30 minutes. The samples were then either quenched or furnace cooled. The samples were examined by resistance and ac susceptibility measurements and by powder X-ray diffraction analyses using the apparatuses and methods we described previously.\(^9,10\)

Figure 1 shows resistance-temperature curves for nominal samples \((\text{TI}_{1.2}\text{Sr}_{2.8}\text{Pr}_{0.4})\text{Cu}_{2}\text{O}_{7}\) (sample A) and \((\text{TI}_{0.9}\text{Pb}_{0.25})(\text{Sr}_{2.8}\text{Pr}_{0.4})\text{Cu}_{2}\text{O}_{7}\) (sample B). These two samples were prepared in the same batch. Although they exhibited PACS Nos.: 74.10 + v, 74.70.Ya.
THERMOELECTRIC POWER OF Tl-Ca-Ba-Cu-O AND Pr-Tl-Sr-Ca-Cu-O HIGH Tc SUPERCONDUCTORS


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The resistance and the thermoelectric power of thallium based high T, superconductors Tl-Ca-Ba-Cu-O and Pr-Tl-Sr-Ca-Cu-O have been measured in the temperature interval 77-300 K. The resistive behaviour of Tl-Ca-Ba-Cu-O is found to be metallic while that of Pr-Tl-Sr-Ca-Cu-O shows a mixed metallic and semiconductive behaviour. The thermoelectric power of both superconductors is positive throughout the temperature interval. The thermoelectric power of the Tl-Ca-Ba-Cu-O superconductor decreases linearly with increasing temperature above the superconducting transition temperature, T,, below which it is zero. The thermoelectric power of the Pr-Tl-Sr-Ca-Cu-O sample shows a maximum near 180 K. The temperature dependence of the thermoelectric power of these samples, above T,, is quite different than that observed for RBa2Cu3O7- phase.

INTRODUCTION

AFTER THE discovery [1] of RBa2Cu3O7- phase, high Tc superconductors with Tc = 90 K where R stands for a rare earth element, a higher Tc of about 100-125 K was obtained in Tl-Ca-Ba-Cu-O superconductors [2]. In particular, Tl2Ca2Ba3Cu4O10 was found to have a Tc of 120-125 K. Recently, a new family of thallium oxide based superconductors, R-Tl-Sr-Ca-Cu-O, have been synthesized with Tc between 80 and 90 K [3]. In this series the Pr-Tl-Sr-Ca-Cu-O system is the first oxide superconducting system containing Pr with Tc above 77 K.

The structure of thallium based oxide superconductors is tetragonal and consists of double, for Tl2Ca2Ba2Cu3O8, or triple, for Tl3Ca3Ba3Cu3O10, CuO2 sheets, with Cu in square planar coordination, stacking alternately with sheets of Ba ions and double sheets of Tl-O atoms, and with Ca between Cu-O sheets [4]. Neutron diffraction results [5] indicate a possible substitution of Ca on the Tl sites and vice versa in Tl2Ca2Ba2Cu3O8 (referred to hereafter as the 2223 phase), and only Ca substitution on the Tl sites in Tl2Ca3Ba2Cu4O10 (referred to hereafter as the 2223 phase). Appreciable disorder of the oxygen atoms in the Tl-O sheets was observed for both compounds, and evidence of a small oxygen deficiency in the 2223 Tl compound was found (x = 9.86 instead of 10, where x is the number of oxygen atoms). Unlike RBa2Cu3O7- phase superconductors, there are no Cu-O chains in Tl2Ca-Ba-Cu-O superconductors. Thus, Cu-O planes seem to be the primary requirement for superconductivity in the cuprate superconductors. Further, unlike RBa2Cu3O7- superconductors, the oxygen content in Tl2Ca-Ba-Cu-O superconductors remains very close to the stoichiometric composition. This difference in structure as well as absence of oxygen deficiency is expected to result in different behaviour of some important physical properties of Tl2Ca-Ba-Cu-O superconductors in comparison with those of RBa2Cu3O7- phase superconductors.

Electronic transport properties of RBa2Cu3O7- phase, in particular those of YBa2Cu3O7- phase, superconductors have been investigated extensively to understand the normal state behaviour and to obtain some clue to the possible interaction responsible for superconductivity at such high temperatures. There have been very few reports on electronic transport properties of Tl2Ca-Ba-Cu-O superconductors. Besides the usual resistance measurements to determine the resistive
JOSEPHSON JUNCTIONS WITH BULK YBa2Cu3O7-x, Bi2Sr2CaCu2Oy, AND Tl2Ca2Ba2Cu3O10+x

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Abstract

The characteristics of point contacts with combinations of Pb, YBa2Cu3O7-x (YBCO), Bi2Sr2CaCu2Oy (BSCCO), and Tl2Ca2Ba2Cu3O10+x (TCBCO) have been measured in a shielded liquid helium dewar. By forming several junctions of a kind we have extracted typical features of the current-voltage characteristics for each combination. Zero-voltage currents were observed in all cases. Diffraction patterns in the dependence of the critical currents on the applied magnetic field were found in some junctions of each kind. Therefore electron-pairs rather than single electrons are responsible for the current transport in all three oxide superconductors mentioned above. For point contacts using the high-Tc materials only, both homo- and hetero-junctions were investigated. We observed Josephson effects above liquid nitrogen temperatures. Whereas YBCO and TCBCO were found to perform very similarly, junctions with BSCCO yielded considerably different results. All junctions behaved like weak link bridge structures.

Introduction

Superconducting point contacts are realized by pressing a sharp piece of superconducting material against a flat one. The resulting structure depends strongly on the mechanical properties of the material as well as the mechanical pressure between them; therefore the underlying physics is, in general, not well defined. The two superconductors are usually linked by several paths, either metallic or through oxide barriers. In spite of the uncertain weak coupling mechanism, point contact structures have been used extensively in the past and play an important role in applications. Point contacts can be readily formed with various materials. We studied point contacts with electrodes made of Pb, YBCO, BSCCO, or TCBCO in various combinations. By forming several point contacts of a kind we could observe features which were common to all junctions of a particular combination of electrodes. In this way we were able to compare junctions formed with the above-mentioned oxide superconductors qualitatively and to some extent also quantitatively.

The superconducting compounds

Both the YBCO and the BSCCO samples were made at the University of Colorado. They showed transition temperatures (R=0) of 94 K and 74 K respectively. The TCBCO samples were made at the University of Arkansas and exhibited a Tc of 125 K.

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Preparation of high $T_c$ Ti-Ba-Ca-Cu-O thin films by pulsed laser evaporation and $\text{Ti}_2\text{O}_3$ vapor processing

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Ti-Ba-Ca-Cu-O superconducting thin films with zero-resistance temperatures up to 115 K have been prepared using a $\text{Ti}_2\text{O}_3$ vapor process on Ba-Ca-Cu-O precursor thin films. The Ba-Ca-Cu-O thin films were made by laser deposition on Y-stabilized $\text{ZrO}_2$ substrates. This technique minimizes problems caused by the toxicity of $\text{Ti}_2\text{O}_3$, and its subsequent decomposition to the volatile and toxic $\text{Ti}_2\text{O}$ upon heating. Therefore, it may have practical application in the fabrication of high $T_c$ Ti-Ba-Ca-Cu-O superconducting thin-film devices.

With the advantages of ease of formation, the highest temperature (120 K) Ti-Ba-Ca-Cu-O superconductors may be the first superconductors for practical commercial applications at liquid-nitrogen temperatures. However, the high toxicity of the thallium compounds commonly used in superconductor preparation has introduced safety concerns in the fabrication of Ti-based superconductors. In order to alleviate this problem, we have developed a $\text{Ti}_2\text{O}_3$ vapor process, which consists of two steps: (a) preparation of Ba-Ca-Cu-O precursors by pulsed laser evaporation, and (b) $\text{Ti}_2\text{O}_3$ vapor processing of the precursors. Vapor processing has produced high quality Ti-Ba-Ca-Cu-O superconductors in bulk, thick wire, and thick-film form. In this letter we report that we have successfully used these techniques for fabricating Ti-Ba-Ca-Cu-O superconducting thin films with zero-resistance temperatures up to 115 K, which is much higher than that previously reported by Qiu and Shih using a similar processing method.

A Ba-Ca-Cu oxide target with a given nominal composition was prepared using the method described in Ref. 1. The oxide film was then deposited by laser deposition onto a Y-stabilized $\text{ZrO}_2$ substrate at 20 °C using a frequency-doubled Nd-YAG laser operating at 523 nm and 10 Hz, forming a Ba-Ca-Cu-O thin film with a thickness of 2–3 μm. This precursor thin film was subjected to a $\text{Ti}_2\text{O}_3$ vapor process similar to that described in Ref. 1. Briefly, a platinum boat containing a small amount of $\text{Ti}_2\text{O}_3$ (typically 0.1–0.2 g) was placed in a quartz boat. The Ba-Ca-Cu-O precursor thin film was then put above the platinum boat. The quartz boat with the contents was put into a tube furnace, which had been heated to 900 °C and was heated for about 3 min in flowing oxygen followed by furnace cooling.

The as-deposited film was a dull black color and an x-ray diffraction scan of the film did not exhibit any peaks other than that of the substrate, indicating that the precursor film was amorphous or extremely fine grained. After $\text{Ti}_2\text{O}_3$ vapor processing, a superconducting thin film was formed. Films deposited from a $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ target will be designated by a Ti-233 prefix. Figure 1 shows the temperature dependencies of resistance for a $\text{Ti}_2\text{O}_3$ vapor-processed Ti-223 film and a $\text{Ti}_2\text{O}_3$ vapor-processed Ti-233 film. Their zero-resistance temperatures are 115 and 104 K, respectively.

The superconducting behavior of vapor-processed thin films depends strongly on processing conditions. The resistance of film Ti-223B as shown in Fig. 2 reached zero only at 80 K since it was heated at too high a temperature (about 920 °C) for 3 min. The film Ti-233B did not show a transition above liquid-nitrogen temperature as seen in Fig. 2. This film was heated at too low a temperature (850 °C) and for too short a time (2 min). After reheating at 900 °C for 3 min, this film reached zero resistance at 104 K, as also seen in Fig. 2. This zero-resistance temperature is identical to film Ti-233A, which underwent a single thallation step.

An x-ray diffraction scan of sample Ti-223A is shown in Fig. 3. The scan shows that the film is multiphase with a c-axis orientation. The dominant phase is the $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ with the indexed (001) peaks corresponding to a lattice parameter of $c = 29.2$ Å. The $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ phases are also

![Figure 1](image_url)
SUPERCONDUCTIVITY ABOUT 120 K IN THE TI-Bi-Sr-Ca-Cu-O SYSTEM

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A number of the samples in the TI-Bi-Sr-Ca-Cu-O system were prepared by a solid state reaction method and were characterized by X-ray powder diffraction, resistivity and AC magnetic susceptibility measurements. A multi-phased sample with nominal composition TlBiSrCaCuO10 is superconducting with a $T_c$ (onset) = 119 K and $T_c (R=0) = 106$ K. X-ray diffraction analysis of the samples shows that the crystal structure of the 120 K superconducting phase is different from that of known TI-based and Bi-based superconducting compounds. Compared with the lead-doped Bi-Sr-Ca-Cu-O compounds, TI-Bi-Sr-Ca-Cu-O compounds have an advantage of easier formation.

1. Introduction

Elemental composition of the high-$T_c$ materials, from La-Sr-Cu-O, Y-Ba-Cu-O to Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O, can be described by a general formula:

$$M-A-Cu-O$$

where $M$ represents RE, TI, Pb, Bi or their combinations; $A$ represents the alkaline earth elements Ca, Sr, Ba or their combinations.

We believe that new high-$T_c$ superconductors can be found in the systems described by the formula (1) with new combinations of the elements. Therefore, a complex research project was planned to explore new high-$T_c$ materials within the framework of this formula. Hundreds of samples have been prepared according to the general formula and resistance and AC susceptibility measurements were made to characterize their electronic properties. Initially, we improved the superconducting properties of some previously studied Sr-Ca-Cu-O based materials. A number of interesting results were obtained, for example, achievement of zero resistance temperatures at 58 K and 80 K were obtained in the Tl-Sr-Ca-Cu-O and La-Tl-Sr-Ca-Cu-O materials respectively. The crystal structure of the superconducting phase in the RE-Tl-Sr-Ca-Cu-O system was determined to be of the so-called 1212-type [1]. Superconductivity above 100 K in the TI-Pb-Sr-Ca-Cu-O and TI-Pb-RE-Sr-Ca-Cu-O systems were confirmed; superconductivity with $T_c = 82$ K in the Tb-Pb-Sr-Ca-Cu-O system was observed [2]. We subsequently found a new series of high-$T_c$ ($T_c$ from 40 K to 70 K) compounds in the Tl-RE-Sr-Cu-O system ($RE=La, Pr, Ce$) without calcium [3]. In this communication, we report the preparation, X-ray characterization and superconducting properties of TI-Bi-Sr-Ca-Cu-O compounds with $T_c$ near 120 K. It should be pointed out that a few groups previously studied the superconductors containing both TI and Bi. Halder et al. [4] have obtained a TI-Bi-Sr-Ca-Cu-O compound with a $T_c (R=0)$ at 75 K [4]. Recently, Li and Greenblatt prepared Tl$_{0.3}$Bi$_{0.7}$Sr$_2$CaCu$_2$O$_y$ using Sr$_4$Ti$_2$O$_9$ as a precursor. This compound, with a 1212-type crystal structure, shows a higher $T_c$ (95 K) than that of other known isostructural compounds [5]. The authors speculated that the superconducting temperature is not only the function of the number of Cu-O layers per unit cell, but is also a function of the hole providing capacity of the TI(Bi, Pb)-O coupling sheets in the structure. We tried to prepare the 1223 or 2223 phase in the Tl-Bi-Sr-Ca-Cu-O systems so as to obtain higher $T_c$ compounds in this system.

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DOUBLE-STEP BEHAVIOR OF CRITICAL CURRENT VS. MAGNETIC FIELD IN Y-, BI- AND TI-BASED BULK HIGH-\(T_c\) SUPERCONDUCTORS

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A double step characteristic is observed at 76 K in the transport critical current as a function of magnetic field (10^{-4} T to 10 T) in bulk sintered Y-, Bi- and Ti-based high-\(T_c\) superconducting materials. The low-field, step-like drop in the critical current density \(J_c\) commences at magnetic fields \(B\) between about 0.3 and 2 mT. This is followed by a plateau region of relatively constant critical current extending from about 30 to 300 mT, and then a second drop at fields between about 0.3 and 10 T. These features occur for all three superconductor materials and are interpreted respectively as a self-field/weak-link regime, a remanent percolation path regime and a flux-flow/upper-critical-field regime. The sharpness of the transition of the voltage-current (V-I) characteristic, represented by the transition parameter \(n\) (i.e., \(V \propto I^n\)), has a similar double-step shape as a function of magnetic field directly corresponding to the features of the \(J_c(B)\) characteristic.

1. Introduction

With the recent discovery of Ti- [1] and Bi-based [2] high-\(T_c\) superconductors, the practical question arises as to the character of the transport critical current in bulk samples of these materials. In particular, is the weak link limitation on the transport critical current of the granular \(Y_1Ba_2Cu_3O_{7-\delta}\) system [3-5] at very low magnetic fields (< about 10 mT) as much of a limit as in the more recently discovered higher-\(T_c\) materials? Also, what is the character of the higher-\(T_c\) materials at high fields?

In this article [6], the transport critical current in Ti-, Bi- and Y-based superconductors has been measured over five orders of magnitude of magnetic field from 10^{-4} T to 10 T in a single field sweep. The results show that the transport critical current density, \(J_c\), at liquid-nitrogen temperature in all three material systems shows a similar two-stage drop-off with magnetic field, \(B(\approx \mu H)\); that is, the \(J_c(B)\) dependence has a double-step character. The first drop in \(J_c\) amounts to between about one and two orders of magnitude and occurs at magnetic fields between 0.3 and 30 mT. This common characteristic is interpreted here as evidence for a weak-link limitation on the transport critical current of all three systems. This is followed by a plateau region at magnetic fields between about 30 mT and 0.3 T where \(J_c\) is relatively independent of magnetic field. The value of \(J_c\) in the plateau regime is strongly dependent on the quality of each sample. The second drop in \(J_c\) occurs between about 0.3 and 10 T. We interpret this as a flux-flow/upper-critical-field regime. For the Ti and Bi systems, the drop is much more precipitous than for the \(Y_1Ba_2Cu_3O_{7-\delta}\) (YBCO) system. Finally we show that, for polycrystalline materials, the drop appears to be dominated by the very low values (1-7 T) of the anisotropic upper critical field \(B_{c2}\) (field perpendicular to the Cu-O planes). The implication of these results is that high-\(T_c\) materials may have to
The effect of pressure on high-$T_c$ superconductors was studied by Josephson absorption as a new and very accurate method for determination of the critical temperature. The uncertainty in $T_c$ was less than 0.06 K. We propose our method as a new standard of $T_c$ measurements. The pressure derivative $dT_c/dp$ equals 1.06 K GPa$^{-1}$ for YBa$_2$Cu$_3$O$_{7-d}$ and 2.20 K GPa$^{-1}$ for Ti-Ca-Ba-Cu-O ceramics. Absence of thermal hysteresis was observed. The change of microwave absorption under hydrostatic pressure was also investigated.

2. Experimental details and results

The YBa$_2$Cu$_3$O$_{7-d}$ sample was prepared by the powder method using Y$_2$O$_3$, BaCO$_3$, and CuO powders as starting materials. The powders were well mixed and pulverized in an agate mortar prior to firing at 920°C for 4 h in oxygen. The powders were fired and pulverized repeated twice to improve the homogeneity. The powders were cold pressed into pellets at about 500 MPa, and sintered at 970°C for 4 h in oxygen then cooled in a furnace. The X-ray diffraction peaks show characteristics of a well-crystallized material, with no impurity phases present. The structure was orthorhombic with lattice parameters $a=381.7$ pm, $b=388.7$ pm, $c=1167$ pm, and $\delta=0.15$. This orthorhombicity and absence of EPR Cu$^{2+}$ signal leads to the conclusion that single-phase samples were studied. The multi-phase Ti-Ca-Ba-Cu-O sample was prepared from Ti$_2$O$_3$, Ba(NO$_3$)$_2$, CaO, and CuO using the standard method described in the literature [22-24]. Measurements of microwave Josephson absorption were carried out by means of a new version [12,13] of a high pressure EPR-probe (fig. 1) attached to the EPR RADIO-PAN SE/X spectrometer. The pressure chamber

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130-K Tl-Ca-Ba-Cu-O SUPERCONDUCTORS

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Abstract We have discovered reproducible and stable bulk superconductivity in the Tl-Ca-Ba-Cu-O system above 130 K with zero resistance above 120 K. Magnetic and electronic transport properties including thermoelectric power of the new superconductors are presented. The Tl-Ca-Ba-Cu-O system contains 125-K 2223 (Tl:Ca:Ba:Cu) phase and 105-K 2122 phase, while the Ca-free Tl-Ba-Cu-O system consists of 80-K 2212 phase, suggesting that the addition of each Cu and Ca layer increases transition temperature by about 20 K. We also present recent Josephson junction studies on the 2223 phase showing the existence of electron pair supercurrents and demonstrating weak link behavior at 77K.

INTRODUCTION

Discoveries of 30-K La-Ba-Cu-O superconductor [1] and 90-K Y-Ba-Cu-O superconductor [2] have stimulated a worldwide race for higher temperature superconductors. Breakthroughs were recently made by the discoveries of the 90-K Tl-Ba-Cu-O system [3,4], 110-K Bi-Ca-Sr-Cu-O system [5,6] and 120-K Tl-Ca-Ba-Cu-O system [7-9]. The Tl-Ba-Cu-O system is the first rare earth-free system which reaches zero resistance above liquid nitrogen boiling point [10], while the Tl-Ca-Ba-Cu-O system is the first system which reaches zero resistance above 100 K and has the highest zero-resistance temperature (125 K)". In this paper, we present the preparation procedures and electronic properties of the 120-K Tl-Ca-Ba-Cu-O superconductors. We also discuss Josephson junction studies on Tl-Ca-Ba-Cu-O which show the existence of electron pair supercurrents and weak link behavior at 77K.

PREPARATION

Tl-Ca-Ba-Cu-O superconductive compounds are easy to synthesize; there are many ways to make good-quality superconducting samples. One of typical procedures in preparing the Tl-Ca-Ba-Cu-O samples which we use is the following. Appropriate amounts of Tl2O3, CaO and Ba-Cu oxide (depending on the desired stoichiometry) were completely mixed and ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was then put into a tube furnace which had been heated to 880-910 °C, and was heated for 2-5 minutes in flowing oxygen, followed by furnace cooling to below 200 °C. Quenching in air from 900 °C to room temperature depresses Tc only slightly. A number of samples with different stoichiometry, including a series of samples with nominal compositions of TlzCa2Ba2Cu2Oy+2y+1 with y = 1, 1.5, 2, 3 and

Ultrasonic attenuation measurements on thallium-based high-temperature superconductors


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We report ultrasonic attenuation measurements on thallium-based high-temperature superconductors with a transition temperature near 110 K. Measurements were carried out between 300 K and liquid-nitrogen temperature. Several peaks were observed with one peak appearing near \( T_c \). At the critical temperature, no sharp drop was noted within our experimental resolution. The attenuation increases with decreasing temperature below \( T_c \). Similar behavior of attenuation measured in Y-based compounds was also observed.

Since the discovery of high-temperature superconductivity, several groups reported measurements of ultrasonic attenuation in both La compounds and Y-based superconductors. Many theories have been suggested to understand the behavior of both systems. None of the reported experimental results show a sharp drop of attenuation near \( T_c \) as would be expected in a normal phonon-mediated BCS-type superconductor. After the discovery of the thallium-based superconductors by Sheng and Hermann, extensive studies were carried out to characterize these new compounds. No measurements of ultrasonic attenuation on thallium-based superconductors have been previously published although preliminary results have been presented. The present work reports measurements of ultrasonic attenuation on TI-based superconductors between 300 K and liquid-nitrogen temperature.

The previously reported ultrasonic attenuation measurements do not exhibit a sharp drop near the transition temperature as predicted by the BCS theory. Most previous work on Y-based superconductors finds that the ultrasonic attenuation generally decreases as the temperature is decreased below 150 K. Near \( T_c \), peaks are often observed while in only two cases a clear minimum is observed. (Ref. 7 has a peak at 10 MHz and a minimum at 30 MHz).

The samples studied were prepared by mixing appropriate amounts of CaO, BaCO\(_3\), and CuO. These powders were mixed and heat treated for 24 h to form the precursor \( \text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x \). \( \text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x \) was ground and mixed with \( \text{TI}_2\text{O}_3 \). The mixed powder was pressed into pellets of 1.27 cm diameter and 0.7-1.0 cm thickness. Channels were cut into preheated graphite blocks at 890-910 °C, heated for 3-5 min in flowing \( \text{O}_2 \) and furnace cooled to room temperature.

Preliminary analysis showed that the resistance of these samples is zero at 110 K. A standard four-probe resistance measurement on a sample similarly prepared to that sample used in our attenuation measurements is shown in Fig. 1. X-ray analysis of similarly prepared samples showed that they were multiphase with a dominant \( \text{TI}_2\text{Ba}_2\text{Cu}_3\text{O}_x \) phase.

FIG. 1. dc resistance-temperature measurements on a similarly prepared sample to that used for attenuation measurements.

FIG. 2. Temperature dependence of attenuation in a TI-based superconductor. Shown is the cooling down from room temperature to 80 K (open circles) and the warming up from 80 to 220 K (filled circles).
90 K BULK SUPERCONDUCTIVITY IN THE TI-Ba-CE-Cu-O SYSTEM

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Bulk superconductivity at 90 K has been observed resistively and by AC susceptibility in the Ti-Ba- Ce-Cu-O system. The results are easily reproduced, and the samples are stable. Powder X-ray diffraction data are presented and discussed.

Discoveries of the Ti-Ba-Cu-O and Ti-Ba-Ca-Cu-O superconducting systems [1-5] have led to identification of a number of Ti-based superconducting compounds, including the series Ti_{m-1}Ba_{2}Ca_{n-1}Cu_{2}O_{1.5m+2n+1} with m=2 [6-9] and with m=1 [10,11], and n=1-5 [6-11]. The Ti_{2}Ba_{2}CaCu_{2}O_{6.8} phase has the highest reproducible zero resistance temperature of 125 K to date [4,5,9]. In order to clarify the high T_c oxide superconducting mechanism and search for new and even higher temperature superconducting systems, we have carried out extensive elemental substitutions for the Ti-based superconducting systems. In a set of experiments, we found that when Ca^{2+} in the Ti-Ba-Ca-Cu-O system is totally replaced by Y^{3+}, the new Ti-Ba-Y-Cu-O system forms a semiconductor TiBa_{2}YC_{2}O_{6.3} (1212 phase). Since Ti-Ba_{2}CaCu_{2}O_{5.5} and 1212 phases in some other systems are superconducting, we have replaced Y^{3+} in the Ti-Ba-Y-Cu-O system with Ce^{4+}, to study the substitution effects of a 4+ valence rare earth on electronic properties and structure of the system. As a result, we found that the Ti-Ba- Ce-Cu-O system is superconducting at 90 K. The results are easily reproduced, and the samples are stable in ambient atmosphere. In this paper, we report preparation procedure, resistance and AC susceptibility measurements, and powder X-ray diffraction results for the new superconducting system.

The Ti-Ba-Ce-Cu-O samples were prepared using high-purity Ti_{2}O_{3}, BaO, CeO_{2}, and CuO. In a typical procedure, appropriate amounts of Ti_{2}O_{3}, BaO, CeO_{2}, and CuO were completely mixed, ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was put in an alumina crucible. The crucible and its contents were put in a tube furnace, which had been heated to 900-925°C, and heated in flowing O_{2} for about 3-5 minutes, followed by furnace cooling. Nominal Ti_{2.2}Ba_{2}CeCu_{2}O_{6.8} samples prepared using the above procedure are superconducting at 90 K. The samples have a dark grey color, and are dense. Superconducting behavior of the samples is sensitive to both heating temperature and heating duration. However, the above procedure does change significantly T_{c} content, for example, Ti in a nominal Ti_{2.2}Ba_{2}CeCu_{2}O_{6.8} sample, after processing, decreases from 2.2 to about 1.75, assuming that Ba, Ce, and Cu remain unchanged. Quenching depresses T_{c} only slightly. Samples prepared in Ar atmosphere are not superconducting.

Resistance (AC, 27 Hz) was measured by the standard four-probe technique with silver paste contacts. AC (27 Hz) susceptibility was measured using the technique similar to that by Norton [12].
PREPARATION AND CHARACTERIZATION OF UNUSUAL LEVITATION Tl–Ba–Ca–Cu–O SAMPLES


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A preparation procedure for the Tl–Ba–Ca–Cu–O superconducting samples which can be levitated above or beneath a magnet is described. X-ray powder diffraction data for these samples are presented and discussed. Their electronic and magnetic properties are presented. The explanation for the unusual levitation is briefly discussed.

Discoveries of the 90 K Tl–Ba–Cu–O system and the 120 K Tl–Ba–Ca–Cu–O superconducting system have led to the identification of various superconducting compounds and the observation of superconductivity in new Tl–based superconducting systems: Tl–Sr–Ca–Cu–O, Tl–Pb–Sr–Ca–Cu–O and Tl–R–Sr–Ca–Cu–O with R = rare-earths. In addition to this progress, which has contributed to the understanding of the mechanism of high temperature oxide superconductivity and to the search for higher temperature superconductors, an interesting levitation phenomenon — a superconductor may be levitated above, to the side of, or beneath a magnet — has been observed for some Tl–Ba–Ca–Cu–O samples. This kind of levitation is denoted as unusual in order to distinguish it from the normal levitation (only above a magnet). Previous examples of the unusual levitation were achieved for some AgO-doped YBa$_2$Cu$_3$O$_y$ samples. While the rare-earth based superconductors which display this unusual levitation must be doped with silver oxide, the Tl-based superconductors showing this behavior need to be specially prepared. In this letter, we describe the preparation procedure of the unusual Tl-based samples. According to our knowledge, this is the first description of a preparation procedure for high-quality unusual Tl-based samples which can be fabricated with great consistency.
120-K Tl-Ca-Ba-Cu-O BULK SUPERCONDUCTORS

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Abstract We have discovered reproducible and stable bulk superconductivity in the Tl-Ca-Ba-Cu-O system above 130 K, with zero resistance above 120 K. Magnetic and electronic transport properties including thermoelectric power of the new superconductors are presented. The Tl-Ca-Ba-Cu-O system contains the 125-K 2223 (Tl:Ca:Ba:Cu) phase and the 105-K 2122 phase, while the Ca-free Tl-Ba-Cu-O system consists of the 80-K 2021 phase, suggesting that the addition of each Cu and Ca layer increases the transition temperature by about 20 K.

INTRODUCTION

Discoveries of the 30-K La-Ba-Cu-O superconductor [1] and the 90-K Y-Ba-Cu-O superconductor [2] have stimulated a worldwide race for higher temperature superconductors. Breakthroughs were recently made by the discoveries of the 90-K Tl-Ba-Cu-O system [3,4] the 110-K Bi-Ca-Sr-Cu-O system [5,6] and the 120-K Tl-Ca-Ba-Cu-O system [7-9]. The Tl-Ba-Cu-O system is the first rare earth-free system which reaches zero resistance above liquid nitrogen boiling point, while the Tl-Ca-Ba-Cu-O system is the first system which reaches zero resistance above 100 K and has the highest zero-resistance temperature (125 K). In this paper, we present the preparation procedures and some properties of the 120-K Tl-Ca-Ba-Cu-O superconductors.

PREPARATION

Tl-Ca-Ba-Cu-O superconductive compounds form easily; there are many ways to make good-quality superconducting samples. One of the typical procedures in preparing the Tl-Ca-Ba-Cu-O...
Superconductivity above 77 K in the \(R\)-Ti-Sr-Ca-Cu-O system (\(R\) represents rare earths)

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Superconductivity at 80–90 K has been resistively and magnetically observed in the \(R\)-Ti-Sr-Ca-Cu-O system (\(R\) represents the rare earths including Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and excelling Ce) in which five metal elements all are required for the superconductivity. In particular, the \(Pr\)-Ti-Sr-Ca-Cu-O system and \(Tb\)-Ti-Sr-Ca-Cu-O system are the first superconducting systems above 77 K in which \(Pr\) or \(Tb\) are required for the superconductivity. We believe that even higher critical temperatures may be achieved by optimizing the starting composition and preparation conditions, and/or by further elemental substitutions.

Discoveries of the Ti-based superconducting systems\(^{1-3}\) have provided increased \(T_c\), with zero-resistance temperatures as high as 125 K.\(^{4-7}\) A number of Ti-based superconducting compounds have been identified, including the series \(Ti_mBa_2Ca_{n-1}Cu_nO_{1+m+2n}\) with \(m=2\) (Refs. 6–11) and 1,\(^{12,13}\) and \(n=1-4,\)\(^{8-13}\) The \(T_c\) of these compounds increases with \(n\) as well as \(m\). These trends have stimulated a strong search for higher \(T_c\)-Ti-based superconductors by increasing \(n\) and/or \(m\). On the other hand, search for new and even higher temperature Ti-based superconducting systems has been also widely carried out. In extensive elemental substitutions, we have observed superconductivity at 20 and 70 K in the Ti-Sr-Ca-Cu-O system.\(^{14}\) Although a sharp drop in resistance at about 100 K was observed in our early experiments and a similar superconductivity was reported by other groups,\(^{15,16}\) these results are difficult to reproduce, suggesting that the formation of this high-temperature superconducting phase is very sensitive to preparation procedure. Recently, Subramanian et al.\(^{17}\) found that addition of Pb into Ti-Sr-Ca-Cu-O system results in formation of high temperature Ti-Pb-Sr-Ca-Cu-O superconducting phases. Two phases, with \(T_c\) 80–90 K for \((Ti_0.3Pb_0.7)Sr_2CaCu_3O_7\) and 120 K for \((Ti_0.5Pb_0.5)Sr_2Ca_2Cu_3O_7\), have been identified. We have obtained similar results.\(^{18}\) In this paper, we report superconductivity at 80–90 K in the Ti-Sr-Ca-Cu-oxide systems with \(R\) representing the rare earths including Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. In these systems, five metal elements all are required for the 80–90 K superconductivity. In particular, the \(Pr\)-Ti-Sr-Ca-Cu-O system and \(Tb\)-Ti-Sr-Ca-Cu-O system are the first superconducting systems above 77 K in which \(Pr\) or \(Tb\) are required for the superconductivity. We believe that higher \(T_c\) may be achieved by optimizing starting composition and preparation conditions. We also believe that new, even higher temperature superconducting systems may be discovered by further elemental substitutions for these systems.

The Ti-Sr-Ca-Cu-oxide samples were prepared using high-purity \(Ti_2O_3\), \(SrCO_3\), \(CaCO_3\), \(CuO\), and rare-earth oxides (\(R_2O_3\) with exceptions of \(CeO_2\) and \(Tb_2O_3\)). First, appropriate amounts of \(SrCO_3\), \(CaCO_3\), and \(CuO\) were mixed and ground. The mixture was heated at 950°C in air for at least 24 h with several intermediate grindings. The resulting \(Sr-Ca-Cu-O\) powder served as master material. In a typical procedure, appropriate amounts of \(Sr-Ca-Cu-O\) powder, \(Ti_2O_3\), and a rare-earth oxide were mixed, ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1–2 mm. The pellet was put into a furnace, which had been heated to 900°C, and was heated in flowing oxygen for 5 min, followed by furnace cooling. Both low-frequency ac resistance and dc resistance were measured by the standard four-probe technique with silver-paste contact. Low-frequency (5-kHz) ac susceptibility was measured using the technique of Norton.\(^{19}\)

Figure 1 shows ac resistance versus temperature curves down to 77 K for samples whose starting compositions were given by \(RTh_2Sr_2CaCu_3O_{11.5}\) (hereafter, \(R\) 1:2:2:2:3), where \(R\) represents the rare earths Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. All samples except \(R=\mathrm{Ce}\) showed a sharp drop in resistance in the range of 80–90 K. Resistance temperature variations in the normal state were linear for most sam-

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** Temperature dependences of the ac resistance for \(R\) 1:2:2:2:3 samples prepared using the typical procedure.
HIGHEST TEMPERATURE (120 K) Tl-Ba-Ca-Cu-O SUPERCONDUCTING SYSTEM

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Abstract The highest temperature (120 K) Tl-Ba-Ca-Cu-O superconducting system comprises a number of superconducting compounds. Tl-Ba-Ca-Cu-O superconductors are easily made. The structure, electronic and magnetic properties are presented. An unusual levitation phenomenon, in which the Tl-Ba-Ca-Cu-O superconductor can be suspended above, below, or to the side of a magnet, is discussed. A new Tl2O3-vapor process for fabricating the Tl-Ba-Ca-Cu-O superconductors is described.

Introduction

Discoveries of 30-K La-Ba-Cu-O superconductor [1] and 90-K Y-Ba-Cu-O superconductor [2] have stimulated a worldwide race for new and even higher temperature superconductors. Breakthroughs were made by the discoveries of the 90-K Tl-Ba-Cu-O system [3,4], 110-K Bi-Sr-Ca-Cu-O system [5,6] and 120-K Tl-Ba-Ca-Cu-O system [7-9]. Recently, high temperature superconductivity was also observed in the Tl-Sr-Ca-Cu-O system [10-12], and in the M-Tl-Sr-Ca-Cu-O with M = Pb [13,14] and rare earths [15]. In this paper, we present preparation procedures, structure, and some properties of the 120-K Tl-Ba-Ca-Cu-O superconductors. We discuss an unusual levitation phenomenon of the Tl-Ba-Ca-Cu-O superconductor due to flux pinning [16]. Finally, we present a new Tl2O3-vapor-process [17] which allows the highest temperature Tl-Ba-Ca-Cu-O superconductors to be easily made in the forms of complex bulk components, wires and fibers, and thick and thin films, and minimizes problems caused by toxicity and volatility of Tl starting compounds.

Preparation

Tl-Ba-Ca-Cu-O superconducting compounds form easily; there are many ways to make good-quality superconducting samples. One of the typical procedures in preparing the Tl-Ba-Ca-Cu-O samples which we use is the following. Ba-Ca-Cu-oxides are first prepared using the method similar to that we previously developed for preparation of Ba-Cu-oxides [18,19]. Appropriate amounts of BaCO3, CaO (or CaCO3), and CuO are mixed, ground, and heated at 925-950 °C in air for 24-48 hour with several intermediate grindings. The resulting uniform black material is ground and served as master material. Appropriate amounts of Tl2O3 and Ba-Ca-Cu oxide (depending on the desired stoichiometry) are completely mixed and ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet is then put into a tube furnace which had been heated to 880-910 °C, and is heated for 2-5 minutes in flowing oxygen, followed by furnace cooling to below 200 °C.

Structure

The Tl-Ba-Ca-Cu-O system can form a number of superconducting phases. Two phases, Tl2Ba2Ca3Cu3O10+x (2223) and Tl2Ba2Ca1Cu2O8+y (2212), were first identified [20]. The 2223 superconductor has a 3.85 x 3.85 x 36.25 Å tetragonal unit cell. The 2212 superconductor has a 3.85 x 3.85 x 29.55 Å tetragonal unit cell [20,21]. The 2223 phase is related to 2212 by addition of extra calcium and copper layers. In addition, the superconducting phase in the Ca-free Tl-Ba-Cu-O system is Tl2Ba2Cu6+x (2201) [20,22]. Fig. 1
Effects of Ag Addition to the Ti - Ba - Ca - Cu - O Superconducting System

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The electronic and structural properties of Ti - based superconductors with AgO added in the range from 2% to 20% by weight are studied. In all cases AgO addition decreases the amount of superconducting phase produced. Small amounts of AgO addition appear to slightly increase zero resistance temperatures and in the case of the 2% sample, dramatically increase the critical current. In samples with larger amounts of AgO addition unreacted Ca2Ba2Cu3O7 is observed as well as silver metal. The bulk resistivity of all the samples is greater than an undoped control sample with the exception of the 20% sample with a resistivity of 1/7 of the control sample. In all cases silver oxide addition did not destroy superconductivity.

I) Introduction

The development of technological applications that incorporate the recently discovered YBa2Cu3Oy (YBCO), Bi-Pb-Ca-Cu-O (BPCCO), and Tl-Ba-Ca-Cu-O (TBCCO) superconducting

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SUPERCONDUCTIVITY ABOUT 120 K IN THE TI-Bi-Sr-Ca-Cu-O SYSTEM

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A number of the samples in the Ti-Bi-Sr-Ca-Cu-O system were prepared by a solid state reaction method and were characterized by X-ray powder diffraction, resistivity and AC magnetic susceptibility measurements. A multi-phased sample with nominal composition TiBiSr$_2$Ca$_2$Cu$_3$O$_{10}$ is superconducting with a $T_c$ (onset) = 119 K and $T_c$ (R=0) = 106 K. X-ray diffraction analysis of the samples shows that the crystal structure of the 120 K superconducting phase is different from that of known TI-based and Bi-based superconducting compounds. Compared with the lead-doped Bi-Sr-Ca-Cu-O compounds, Ti-Bi-Sr-Ca-Cu-O compounds have an advantage of easier formation.

1. Introduction

Elemental composition of the high-$T_c$ materials, from La-Sr-Cu-O, Y-Ba-Cu-O to Bi-Sr-Ca-Cu-O and Ti-Ba-Ca-Cu-O, can be described by a general formula:

$$M\text{-}A\text{-Cu}\text{-O}$$

where $M$ represents RE, TI, Pb, Bi or their combinations; $A$ represents the alkaline earth elements Ca, Sr, Ba or their combinations.

We believe that new high-$T_c$ superconductors can be found in the systems described by the formula (1) with new combinations of the elements. Therefore, a complex research project was planned to explore new high-$T_c$ materials within the framework of this formula. Hundreds of samples have been prepared according to the general formula and resistance and AC susceptibility measurements were made to characterize their electronic properties. Initially, we improved the superconducting properties of some previously studied Sr-Ca-Cu-O based materials. A number of interesting results were obtained, for example, achievement of zero resistance temperatures at 58 K and 80 K were obtained in the Ti-Sr-Ca-Cu-O and La-Ti-Sr-Ca-Cu-O materials respectively. The crystal structure of the superconducting phase in the RE-Ti-Sr-Ca-Cu-O system was determined to be of the so-called 1212-type [1]. Superconductivity above 100 K in the Ti-Pb-Sr-Ca-Cu-O and Ti-Pb-RE-Sr-Ca-Cu-O systems were confirmed; superconductivity with $T_c=82$ K in the Tb-Pb-Sr-Ca-Cu-O system was observed [2]. We subsequently found a new series of high-$T_c$ ($T_c$ from 40 K to 70 K) compounds in the TI-RE-Sr-Ca-Cu-O system (RE = La, Pr, Ce) without calcium [3]. In this communication, we report the preparation, X-ray characterization and superconducting properties of Ti-Bi-Sr-Ca-Cu-O compounds with $T_c$ near 120 K. It should be pointed out that a few groups previously studied the superconductors containing both Ti and Bi. Haldar et al. [4] have obtained a Ti-Bi-Sr-Ca-Cu-O compound with a $T_c (R=0)$ at 75 K [4].

Recently, Li and Greenblatt prepared Ti$_{0.5}$Bi$_{0.5}$Sr$_2$CaCu$_2$O$_y$ using Sr$_2$Ti$_2$O$_7$ as a precursor. This compound, with a 1212-type crystal structure, shows a higher $T_c$ (95 K) than that of other known isostructural compounds [5]. The authors speculated that the superconducting temperature is not only the function of the number of Cu-O layers per unit cell, but is also a function of the hole providing capacity of the Ti(Bi, Pb)–O coupling sheets in the structure. We tried to prepare the 1223 or 2223 phase in the Ti-Bi-Sr-Ca-Cu-O systems so as to obtain higher $T_c$ compounds in this system.

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Superconductivity at 82 K has been observed by low frequency ac susceptibility and resistance measurements in the Tb-Pb-Sr-Ca-Cu-O system. The powder x-ray diffraction pattern, compared with related published data, can be indexed from an orthorhombic lattice with $a=5.38$ Å, $b=5.42$ Å, and $c=15.71$ Å.
Formation of Ti-Ca-Ba-Cu-O Superconducting Thick Films by Vapor Evaporation of TiO₂ into Rolled Ca₂Ba₂Cu₃Oₓ

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Abstract: Using a roller technique, Ba₂Ca₂Cu₃Oₓ thick film precursors (about 100 microns in thickness) were prepared. These films were then treated by a vapor process using TiO₂ to form superconducting Ti-Ba-Ca-Cu-O films. The superconducting onset temperature of these film is about 120K with a zero-resistance temperature ranging from 91K to 111K. X-ray SEM, and electron microprobe analyses of these films are presented, and, on the basis of these analyses, crystallite growth will be discussed.
Tl-Based Cu-O High Temperature Superconductors

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Abstract. We have discovered reproducible and stable bulk superconductivity in the Ti-Ca-Ba-Ou-O system with zero resistance above 120 K. Magnetic and electronic transport properties including thermoelectric power and critical current of the new superconductors are presented. The Ti-Ca-Ba-Ou-O system can form a number of superconducting compounds, including TlzCa:yBa:z1.5Cu:5n+1 with m = 1 and 2, and n = 1, 2, 3, and 4. The Tc increases with m and n. The 2223 (TlzCa:yBa:z1.5Cu:5n+1) phase has the highest Tc (125 K) to date. We present Josephson junction studies on the 2223 phase showing the existence of electron pair supercurrents and demonstrating weak link behavior at 77 K. We discuss an unusual levitation phenomenon in which the 2223 phase can be suspended, above, below, or to the side of a ring shaped magnet. We also discuss a new Tl-based superconducting system, in which Sr replaces the Ba, the Ti-Ca-Sr-Ou-O system.

INTRODUCTION

Discoveries of 30-K La-Ba-Ou-O superconductor [1], and 90-K Y-Ba-Ou-O superconductor [2] have stimulated a worldwide race for higher temperature superconductors. Breakthroughs were recently made by the discoveries of the 90-K Ti-Ba-Ou-O system [3,4], 110-K Bi-Ca-Sr-Ou-O system [5,6] and 120-K Ti-Ca-Ba-Ou-O system [7-9]. The Ti-Ba-Ou-O system is the first rare earth-free system which reaches zero resistance above liquid nitrogen boiling point, while the Ti-Ca-Ba-Ou-O system is the first system which reaches zero resistance above 100 K and has the highest zero-resistance temperature (125 K). In this paper, we present the preparation procedures and some properties of the 120-K Ti-Ca-Ba-Ou-O superconductors, we discuss unusual levitation phenomena due to flux pinning, and we present Josephson junction studies on Ti-Ca-Ba-Ou-O which show the existence of electron pair supercurrents and weak link behavior at 77 K. We also present preliminary data on a new Ti-based superconducting system, Ti-Ca-Sr-Ou-O.

PREPARATION

Ti-Ca-Ba-Ou-O superconductive compounds form easily; there are many ways to make good-quality superconducting samples. One of typical procedures in preparing the Ti-Ca-Ba-Ou-O samples which we use is the following. Appropriate amounts of TlzOx, CaO and Ba-Ou oxide (depending on the desired stoichiometry) were completely mixed and ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was then put into a tube furnace which had been heated to 800-910 °C, and was heated for 2-5 minutes in flowing oxygen, followed by furnace cooling to below 200 °C. Quenching in air from 900 °C to room temperature depresses Tc only slightly. A number of samples with different stoichiometry, including a series of samples with nominal compositions of TlzCa:yBa:z1.5Cu:5n+1 with y = 1, 1.5, 2, 3 and 4, were prepared. Samples with nominal compositions of TlzCa:yBa:z1.5Cu:5n+1 and TlzCa:yBa:z1.5Cu:5n+1 were also synthesized, all samples readily levitate over a magnetic field. The strong Meissner effect observed is due to both a large volume fraction of superconduct phase and a higher transition temperature. Recently, most samples were prepared using precursor Ba-Ca-Cu-oxides.

STRUCTURE

The Ti-Ca-Ba-Ou-O system can form a number of superconducting phases. Two phases, TlzCa:yBa:z1.5Cu:5n+1 (2223) and TlzCa:yBa:z1.5Cu:5n+1 (2122), were first identified [10]. The 2223 superconductor has a 3.85 x 3.85 x 36.25 Å tetragonal unit cell. The 2122 superconductor, which appears to be structurally related to Bi2CaSr2CuO5+x, has a 3.85 x 3.85 x 29.55 Å tetragonal unit cell [10,11]. The 2223 phase is related to 2122 by addition of extra calcium and copper layers. In addition, the superconducting phase in the Ca-free Ti-Ba-Ou-O system is TlzBa2O3+x [10-12]. Fig. 1 shows schematically the arrangements of metallic atoms in these three Ti-based superconducting phases. The 201 phase has a zero-resistance temperature of about 80 K, whereas the 2122 and 2223 phases have zero-resistance temperatures 108 K and 125 K, respectively [10-15]. It appears that the addition of a Ca and Cu layer increases the
Superconductivity above 40 K has been observed by low frequency ac susceptibility and resistance measurements in the R-TI-Sr-Cu-O system with R = La, Pr, Nd, and Y. Powder x-ray diffraction analyses for a nominal La$_2$Tl$_2$Sr$_2$Cu$_2$O$_{10}$ sample and a nominal Pr$_2$Tl$_2$Sr$_2$Cu$_2$O$_{10}$ sample showed that they were nearly single phase, and can be indexed to a tetragonal unit cell with a = 3.775(2) Å and c = 35.35(2) Å, and with a = 3.762(2) Å and c = 35.34(2) Å, respectively.

Discoveries of the 90 K Tl-Ba-Cu-O system [1,2] and 120 K Tl-Ba-Ca-Cu-O system [3-5] have lead not only to the identification of a number of Tl-containing superconducting compounds, including Tl$_2$Ba$_2$Cu$_2$O$_{6+δ}$ with m = 1-2, and n = 5 [6-11], but also to the discoveries of a series of Sr-Ca-Cu-O-based superconducting systems: the 70 K Tl-Sr-Ca-Cu-O system [12], the 115 K Pb-Tl-Sr-Ca-Cu-O system [13], the 90 K Tl-Ti-Sr-Ca-Cu-O system with R = rare earths [14], and the 70 K Pb-R-Sr-Ca-Cu-O system [15,16].

Further experiments reported in this paper on the 90 K Tl-Ti-Sr-Cu-O system have showed that the Tl-Ti-Sr-Cu-O system (without Ca) is also superconducting at lower temperatures (about 40 K). Unlike the Tl-Ti-Sr-Ca-Cu-O system in which the rare earths do not influence significantly the superconducting behavior, the rare earths in the Tl-Ti-Sr-Cu-O system change greatly the properties of the system. So far only samples with R = La, Pr, Nd, and Y have been observed to be superconducting unambiguously above 15 K. In this paper we present preparation procedures, ac susceptibility and resistance measurements, and powder x-ray diffraction data.

The R-Tl-Sr-Cu-oxide samples were prepared using high-purity Ti$_2$O$_3$, SrO (or SrCO$_3$), CuO and rare earth oxides (REO with exceptions of CuO and Th$_2$O$_3$). Two procedures were used. In one procedure, component oxides with a certain molar ratio were completely mixed, ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was heated in a tube furnace at about 950 °C for 3-5 minutes in flowing oxygen, followed by furnace-cooling or quenching. In a second procedure, a Sr-Cu-O precursor was first prepared by mixing and grinding appropriate amounts of SrCO$_3$ and CuO, and heating at 950 °C in air for at least 24 hours with several intermediate grindings. The resulting Sr-Cu-O powder served as master material. Appropriate amounts of Sr-Cu-O powder, Ti$_2$O$_3$, and a rare earth oxide were mixed, ground and pressed into a pellet. The pellet was heated in a tube furnace at 900 °C for 5 minutes in flowing oxygen, followed by furnace-cooling or quenching.

Resistance (ac, 27 Hz) was measured by the standard four-probe technique with silver paste contacts. AC (500 Hz) susceptibility was measured using the technique similar to that by R.H. Silsbee [17]. Powder X-ray diffraction was carried out with Cu-Kα radiation with use of a DIANID TDM 1057 diffractometer.

Properties of the R-Tl-Sr-Cu-O samples depended strongly on both the rare earths and the preparation procedures. Superconducting samples with R = La and Pr were prepared using both procedures, and superconducting samples with R = Nd and Y were made only using the first procedure. Neither procedure has unambiguously produced superconducting samples with rare earths other than La, Pr, Nd, and Y. Fig. 1 shows resistance-temperature dependences for nominal La$_2$Tl$_2$Sr$_2$Cu$_2$O$_{10}$, nominal Pr$_2$Tl$_2$Sr$_2$Cu$_2$O$_{10}$, and nominal Nd$_2$Tl$_2$Sr$_2$Cu$_2$O$_{10}$ samples. Resistance-temperature variations of these samples are strictly linear in the normal state up to room temperature. The superconducting transitions of the La sample and the Pr sample are fairly sharp.
THE HIGH Tc Ti-Ba-Ca-Cu-O SUPERCONDUCTING SYSTEM

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INTRODUCTION

Discoveries of 30-K La-Ba-Cu-O superconductor [1] and 90-K Y-Ba-Cu-O superconductor [2] have stimulated a worldwide race for new and even higher temperature superconductors. Breakthroughs were made by the discoveries of the 90-K Ti-Ba-Cu-O system [3,4], 110-K Bi-Sr-Ca-Cu-O system [5,6] and 120-K Ti-Ba-Ca-Cu-O system [7-9]. Recently, high temperature superconductivity was also observed in the Ti-Sr-Ca-Cu-O system [10-12], and in the M-Ti-Sr-Ca-Cu-O with M = Pb [13,14] and rare earths [15]. In this paper, we present preparation procedures, structure, and some properties of the 120-K Ti-Ba-Ca-Cu-O superconductors. We discuss an unusual levitation phenomenon of the Ti-Ba-Ca-Cu-O superconductor due to flux pinning [16]. Finally, we present a new Ti$_2$O$_3$ vapor-process [17] which allows the highest temperature Ti-Ba-Ca-Cu-O superconductors to be easily made in the forms of complex bulk components, wires and fibers, and thick and thin films, and minimizes problems caused by toxicity and volatility of Ti starting compounds. Recent results on Ti$_2$O$_3$ vapor-processing of thin film Ba-Ca-Cu-O precursors are included.

PREPARATION

Ti-Ba-Ca-Cu-O superconductive compounds form easily; there are many ways to make good-quality superconducting samples. One of the typical procedures in preparing the Ti-Ba-Ca-Cu-O samples which we use is the following. Ba-Ca-Cu-oxides are first prepared using the method similar to that we previously developed for preparation of Ba-Cu-oxides [18,19]. Appropriate amounts of BaCO$_3$, CaO (or CaCO$_3$), and CuO are mixed, ground, and heated at 925-950 °C in air for 24-48 hour with several intermediate grindings. The resulting uniform black material is ground and served as master material. Appropriate amounts of Ti$_2$O$_3$ and Ba-Ca-Cu oxide (depending on the desired stoichiometry) are completely mixed and ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet is then put into a tube furnace which had been heated to 880-910 °C, and is heated for 2-5 minutes in flowing oxygen, followed by furnace cooling to below 200 °C.

STRUCTURE

The Ti-Ba-Ca-Cu-O system can form a number of superconducting phases.
Main periodic structures are more difficult to synthesize. The main problem in the synthesis is believed to be the synthesis route used so far. Starting with the temperature region in which these structures are found with the approximate composition T12CaBa2Cu3O10+6, it has to react with the remaining Ca compounds. Such a process will take a very long time (days) because of the large particle sizes and the existence of a phase with a c-axis of 4.3 nm. The number of perovskite layers can be increased from 2 to 4 and 3.7-nm phase is readily formed. Extreme care was taken, because of the toxicity of BaO3, CaO, BaCO3, and pressed into pellets of diameter 5 mm and thickness 1.5 mm. The pellets were put into a furnace which had been heated to 880–950°C, and were heated for 2–5 min in flowing oxygen. Finally, the pellets were quenched in air to room temperature by taking them from the furnace or cooled to room temperature in the furnace by turning off the power with the furnace door slightly open or closed. X-ray powder diffraction was done with a Rigaku D/MAX IIB automated diffractometer with a Cu source. Bar-shaped samples measuring 4×1.5×1.5 mm were cut from the pellets for electrical and magnetic measurements.

Seven TCBCO samples with nominal composition T12CaBa2Cu3O10+6 were synthesized under different conditions. Recently, Sheng and Hermann reported the achievement of zero resistance at >100 K in the system Tl2Ca2Ba2Cu3O (TCBCO). Two superconducting phases were immediately identified3 as Tl12Ca2Ba2Cu3O10+6 (2122) and Tl2Ca2Ba2Cu3O10+6 (2223). Here we confirm that zero resistance is achievable above 100 K in 2122-TCBCO synthesized by a fast solid-state reaction, and report a small positive pressure dependence of the transition temperature, as in Bi2Sr2CaCu2O8+δ.

Recently, Sheng and Hermann reported the achievement of zero resistance at >100 K in the system Tl2Ca2Ba2Cu3O (TCBCO). Two superconducting phases were immediately identified as Tl12Ca2Ba2Cu3O10+6 (2122) and Tl2Ca2Ba2Cu3O10+6 (2223). Here we confirm that zero resistance is achievable above 100 K in 2122-TCBCO synthesized by a fast solid-state reaction, and report a small positive pressure dependence of the transition temperature, as in Bi2Sr2CaCu2O8+δ.

Table 5 Schematic representations of the structures of a, CaCu2O2+δ, b, Bi2Sr2Ca2Cu3O10+6, and c, Bi2Sr2Ca2Cu3O10+6. The black dot pattern observed in Fig. 4. The unit cells are indicated by a full drawn line.

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Thermoelectric power of the Ti-Ca-Ba-Cu-O superconductor

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We report measurements of the thermoelectric power of the high-temperature Ti-Ca-Ba-Cu-O superconductor. The data indicate a transition which is centered at 118 ± 3 K, in agreement with magnetic measurements and published resistivity results. The thermoelectric power is positive and, aside from the high transition temperature, is remarkably similar in magnitude and temperature dependence to that of the rare-earth-based oxide superconductors which have been reported previously.

Since the discovery of high-temperature oxide superconductors in 1986 by Bednorz and Müller,1 at least three families of such materials have been identified. The first group, containing La-Ba-Cu-O and its derivatives, exhibits superconductivity in the range of 30–40 K. The second group, discovered by Chu and co-workers,2 is described by R-Ba-Cu-O, where R represents one of the rare-earth elements or yttrium. These materials exhibit transitions in the 90-K range. Recently, a new family has been discovered with even higher transition temperatures in the range of 115–120 K. Remarkably, the new materials do not contain yttrium or any of the rare-earth elements. One type, which has been studied by several workers,3–5 contains the element bismuth. A second type, first announced by Sheng and Hermann,6 and later confirmed by others,7 is distinguished by the presence of thallium. The purpose of this note is to describe recent measurements of the thermoelectric power of this new material.

The samples were prepared at the University of Arkansas from Ba$_2$Cu$_4$O$_7$ and oxides of thallium and calcium. The powders were mixed, ground, pressed into pellets, and then heated to about 900 °C in flowing oxygen for 3 min. The sample was furnace cooled by turning off the furnace for 1 h and then removed. These procedures have been described in more detail in previous publications.5,8

The apparatus and procedures for the thermoelectric power measurements have also been described in an earlier paper.9 A differential method was employed in which a voltage difference is measured across the sample in response to an imposed temperature difference. Two sets of reference leads (Constantan and Chromel) were used and the voltages, after correcting for the thermoelectric power of the leads, were averaged to obtain the final results. The measurements were made in vacuum as the sample slowly warmed from liquid-nitrogen temperature to ambient.

Figure 1(a) shows the thermoelectric power data for a sample with nominal composition Ti$_2$Ca$_2$Ba$_2$Cu$_6$O$_{10.3+X}$. Energy-dispersive x-ray measurements on this sample indicated a composition of Ti$_{12.20}$Ca$_{2.06}$Ba$_{3.14}$Cu$_{3.72}$O$_x$. Figure 1(b) shows thermoelectric power data for a Y-Ba-Cu-O sample for comparison. In either case the normal-state thermoelectric power is positive, indicating dominant hole conduction, and drops rapidly to zero at the superconductive transition. The apparent transition for both samples is somewhat broadened by the temperature difference of several degrees which was imposed during the measurements. The midpoint of the transition was determined to lie at 118 ± 3 K. This is in good agreement with data taken at 1 MHz by a magnetic induction technique10 which showed an onset of screening at about 115 K. The midpoint of the thermoelectric transition for the Y-Ba-Cu-O sample is 93 ± 2 K.

Resistance was measured by the standard four-probe technique using silver-paste contacts. Figure 2 shows the temperature dependence of the resistance for a piece of the sample of Fig. 1(a). From this curve it is seen that the onset of the resistive transition is about 120 K, the midpoint is 110 K, and the sample reaches zero resistance (less than 10$^{-6}$ Ωcm) at 104 K.

At least three separate ranges of temperature-dependent behavior are apparent in the thermoelectric power data of Fig. 1. Below the transition, this quantity is required to vanish on thermodynamic grounds. From the transition temperature to about 175 K in both samples, the thermoelectric power is an increasing function of temperature. Finally, from 175 K to room temperature, we observe a linear decrease with increasing temperature. The pronounced peak near 175 K in the data for both samples is believed to be intrinsic. Careful calibration of the thermoelectric power of the reference leads, as well as measurements on nonsuperconductive materials in this temperature range, have revealed no other explanation for this feature.

Several reports on the thermoelectric powers of oxide superconductors have appeared in the literature.11–17 In
Levitation effects involving high $T_c$ thallium based superconductors

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The thallium based superconductor Tl$_2$Ca$_2$Ba$_2$Cu$_2$O$_{10+y}$ has been shown to exhibit very stable and unusual levitation equilibria in various arrangements involving this material and permanent magnets. Attractive and repulsive forces are evident in experiments in which samples are levitated above and below magnets. Photographs of these experiments and approximate quantitative discussions of the results are given.

The recent discovery of thallium based superconductors $^{1-4}$ with critical temperatures greater than 100 K has stimulated renewed interest in applications of materials with unusual magnetic properties. Of particular interest is the ability of these materials to be suspended or levitated in the presence of permanent magnets or to suspend magnets themselves. Levitation of rectangular magnets over rare-earth based superconductors has been discussed by Hellman et al. $^5$ and by Williams and Matey. $^6$ Hellman et al. $^5$ analyzed and measured the point of equilibrium in the vertical direction for a magnet over a flat rare-earth based superconductor, and they gave a qualitative discussion of the curious horizontal stability. Williams and Matey $^6$ also noted the curious horizontal stability and measured the frequency of torsional and translational motions of a magnet around its horizontal equilibrium above a flat superconductor.

For the thallium based superconductors, even more striking examples of stable levitation occur when either the magnet or the superconductor are suspended. There appears to be a continuous range of stable levitation positions for a magnet above a thallium based superconducting disk, and these disks may themselves be levitated above, to the side of, or below a ring magnet as shown in photographs given in the following. Previous examples of inverted levitation were achieved by Peters et al. $^7$ using a rare-earth based material, but in that case it was necessary to dope the material with silver oxide.

A spinning cylindrical Co-Sm permanent magnet is shown in Fig. 1 suspended above a cylindrical sample of a Tl$_2$Ca$_2$Ba$_2$Cu$_2$O$_{10+y}$ superconductor. The sample was prepared according to Ref. 1. The magnet is magnetized along its axis. A small amount of liquid nitrogen (LN) is maintained in an inverted styrofoam container which supports the sample. The magnet has a diameter and height of 0.3 cm and a mass of 0.167 g. The superconducting sample has a diameter of 0.8 cm and a thickness of 0.1 cm.

The magnet has a range of stable positions which can be achieved by simply forcing the magnet into them. The range of stable positions for the center of the magnet comprises a roughly cylindrical volume which begins at a height of about 0.2 cm above the sample, extends up to about 0.4 cm, and includes all points within about 0.15 cm of the edge of the sample. In other words, the magnet can be placed so that it rotates stably with one end very near the edge of the sample or anywhere in between. In addition, the orientation of the magnet may be set somewhat arbitrarily. At each point it can be tilted to any angle within about 40° of the horizontal and it will usually stay there.

The stability of each position and orientation can be roughly tested by simply picking up the sample while it levitates the magnet and tilting or shaking the sample. Surprisingly, for some positions, the magnet remains near its equilibrium point even when the sample is tilted by more than 45°. The critical angle of repose depends on the orientation and position of the magnet, and provides an easy way to find the horizontal components of force needed to change the equilibrium position given the mass (m) or weight (mg) of the magnet.

$$f_{\text{vertical}} = mg \sin \phi_{\text{vertical}}.$$ (1)

The critical angle and force are greatest when the magnet is centered parallel to the sample and is tilted along its axis. It is also greatest when the point of equilibrium is as close as possible to the surface of the magnet.

The levitation of two disks of the thallium based superconductor by a ring magnet is shown in Figs. 2 and 3. The orientation in each figure can be verified by the falling of the cooled vapor which is visible in the lower part of the photographs. In each case the magnet is gripped in a pair of handheld insulating pliers and is viewed edge-on and the samples appear to be suspended in magnetic pockets. The Co-Sm ring magnet has an outer diameter of 1.9 cm, an inner diameter of 1.0 cm, and it is 0.6 cm thick. The suspended thallium based

![Image](https://example.com/image.png)  
**FIG. 1.** Rotating magnet suspended above a thallium based superconductor behaves like a frictionless bearing.
Structural and elemental analysis of melt-processible high-temperature superconductors by surface science and x-ray diffraction measurements

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We report the results of scanning electron microscopy (SEM), microprobe analysis (wavelength dispersive and energy dispersive spectroscopies), secondary-ion mass spectroscopy (SIMS), and x-ray diffraction measurements on a series of melt-processed high critical-temperature superconductors. The superconductors were synthesized through a melt reaction between $\text{TbBa}_2\text{Cu}_3\text{O}_7-\delta$ and nonstoichiometric rare-earth Ba-Cu-O oxides. The melt-processed samples are dense, largely void-free superconductors with critical temperatures in the 90–95 K range. Microprobe and SIMS data show the absence of Tb in surfaces of the interiors of samples which had been fractured to expose the interior regions. Comparative microprobe and SEM data are included for conventionally prepared sintered samples. Comparative x-ray diffraction studies are presented which show that the melt-processed samples have diffraction patterns nearly identical to those of sintered (rare earth)Ba$_2$Cu$_3$O$_7-\delta$ samples. In two of the three Y-based melt-processed superconductors studied, the compound stoichiometry from microprobe analysis is $Y_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The evidence presented indicates that the TbBa$_2$Cu$_3$O$_{7-\delta}$ decomposes during the melt reaction.

I. INTRODUCTION

The recent discovery of superconductors whose critical temperature exceeds 90 K has caused a scientific rush to find processible materials capable of carrying large current densities and of being manufactured into useful superconducting components for magnets, power transmission cables, levitated vehicles, and a plethora of other applications only now being conceived.

We have discovered two melt processes that produce dense rare-earth-based high-temperature superconductors that are void free. This paper reports the characterization of these superconductors by scanning electron microscopy (SEM), microprobe analysis, secondary-ion mass spectroscopy (SIMS), and x-ray diffraction (XRD). Resistivity-temperature variations showing the superconducting critical temperatures are also included.

II. EXPERIMENT

The bulk superconductors were formed in a melt process in which molten $\text{TbBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was reacted at 950 °C with sintered (rare earth)Ba$_2$Cu$_3$O$_{7-\delta}$, where the rare earths studied to date include Y, Ho, Nd, Sm, Gd, Er, Tm, Yb, and Lu. Since Y is typical of the rare earths studied, we emphasize here the measurements on Y-based compounds as sintered starting materials. To form the $\text{TbBa}_2\text{Cu}_3\text{O}_{7-\delta}$, mixtures of Tb$_3$O$_7$, BaCO$_3$, and CuO powders were ground in an agate mortar and heated in air at 890–910 °C for 6–8 h in a tube furnace to prepare a powder of nominal composition $\text{TbBa}_2\text{Cu}_3\text{O}_7$. To form the Y-based starting compounds, mixtures of Y$_2$O$_3$, BaCO$_3$, and CuO were treated similarly to form a powder of nominal composition $Y_{1.2}\text{Ba}_2\text{Cu}_3\text{O}_{6.8}$. The heated mixtures were then reground and, in certain cases, pressed into pellets of diameter 1 or 1/4 in. In one set of experiments, the powdered Tb and Y compound were pressed separately into pellets and heated (Tb pellet on top of Y pellet) to 920–960 °C in flowing O$_2$ for 12–24 h in a tube furnace. The sample was then cooled in the furnace to 200 °C in 1–2 h before being brought to room temperature.

The Y pellet is initially green, the Tb pellet yellow-brown. After the melt reaction and cooling, the interfacial melt-recrystallized layer (several millimeters thick) is black. According to a weight balance experiment, if the Y compound had melted uniformly, the melt-recrystallized superconductor would have a composition of $\text{Tb}_{0.71}Y_{0.29}\text{Ba}_{2.11}\text{Cu}_3\text{O}_7$ (we discuss decomposition of the Tb compound in a later section). We have found that elemental Cu can also replace the CuO in the starting compound, and that a powder of the Y (or another rare earth) compound can be substituted for a pellet in the process. The resultant melt-recrystallized portions were cut away from any unmelted portions of the Y pellet, as necessary.

The SEM measurements were made on a PHI model 600 scanning auger microprobe having a base pressure of $1 \times 10^{-10}$ Torr. SIMS measurements were made with a Perkin-Elmer/Physical Electronics SIMS II spectrometer. An electrostatic extraction lens was used at the front end of the quadrupole to increase sensitivity.

Microprobe analysis by wavelength dispersive spectroscopy was performed using a Cameca MBX spectrometer at an incident energy of either 10 or 15 keV. (The latter is sufficient to stimulate Tb emission, but too energetic for highly accurate oxygen analysis.)

The analysis point was disk shaped with a diameter of 20 μm. Five or six randomly chosen (unless specified otherwise) points were sampled on each surface studied.
from that region. However, if \( Z_0 \) is increased further, to
9 km, the corresponding spectrum is quantitatively incompatible with the data. Its interest becomes too large. The curve shows that mixing ratios similar to those measured in summer can only extend to altitudes around 18 km if the mixing ratio decreases unrealistically rapidly at higher altitudes. Curve B is an example of an intermediate case. The three curves cross at 35 km; at this altitude they have a mixing ratio which is a factor 5 less than the summertime measurements.\(^1\) A factor of 2 less than predicted by the Solomon and Garcia model, and a factor of 6 less than the model results reported. Curve A, which has the largest mixing ratios of the three above 25 km, is less stable than the summer measurements and the Jones and Pyle model factor of 10 at 25 km, and less than the Solomon and Garcia model by a factor of 3. Curves A-C are upper limits in the sense we cannot rule out lower mixing ratios because of possible instrumental curvature.

We have separately analysed the average of the data measured in the event of 23 and 24 September, and find that the

\[
\text{largest mixing ratios of the three above 25 km, is less than}
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6 h a peak mixing ratio of -40 \( \text{ppb.v.} \) for an event of 23 and 24 September, and find that the

\[
\text{shape is consistent with the Solomon and Garcia model, and a}
\]

factor of 6 less than the model results reported. Curve A, which has the largest mixing ratios of the three above 25 km, is less stable than the summer measurements and the Jones and Pyle model factor of 10 at 25 km, and less than the Solomon and Garcia model by a factor of 3. Curves A-C are upper limits in the sense we cannot rule out lower mixing ratios because of possible instrumental curvature.

We present data showing chlorine toable here further demonstrate the unusual and unexpected nature of the Antarctic springtime stratosphere.

We thank the NSF's Division of Polar Programs for its support through all phases of our Antarctic work, and the many individuals in Antarctic Services, Inc., the US Navy Support Force and the NSF whose interest and enthusiasm smoothed our way. We thank Dr R. L. Jones for supplying us with information on the trajectory of air over McMurdo during 23-24 September 1986, and NASA's Upper Atmospheric Research Program and the Chemical Manufacturer's Association for the support which made it possible to carry out this research.

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Superconductivity in the rare-earth-free Tl-Ba-Cu-O system above liquid-nitrogen temperature

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The initial discovery by Bednorz and Muller\(^1\) of 35-K superconductivity in the La-Ba-Cu-O system has stimulated worldwide activity in searching for higher-temperature superconductors. Elemental substitution has proved to be most effective in raising transition temperature. Substitution of Sr for Ba has produced 40-K superconductivity\(^2\), and substitution of Y for La has produced a new high-temperature superconductor with transition temperature above liquid-nitrogen temperature\(^3\). A class of superconducting compounds of the form RBa\(_2\)Cu\(_3\)O\(_x\) has been explored by further substitutions of other rare earths (Y is considered in the rare-earth [R] category here) for Y\(^{145}\). To date, a rare earth, an alkaline earth, copper and oxygen have been required for high-temperature superconductors\(^4\). \(^5\). (Zhang et al.\(^6\) reported 90-K superconductivity in the Th-Ba-Pb(Zr)-Cu-O system. Pan et al.\(^7\) reported 50-K superconductivity in the Y-Ba-Ag-O system. Th is a member of the actinide series which belongs to the same Group 3B in the periodic table as the lanthanide series and Ag...
Bulk superconductivity at 120 K in the Tl–Ca/Ba–Cu–O system

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The discovery of 30-K superconductivity in the La–Ba–Cu–O system\(^1\) and 90-K superconductivity in the Y–Ba–Cu–O system\(^2\) stimulated a worldwide search for even higher-temperature superconductors. Unfortunately, most of the higher-temperature transitions reported in the past year have proved to be unstable, irreproducible, or not due to bulk superconductivity\(^3\)–\(^5\). Recently, we and co-workers\(^6\)–\(^8\) reported superconductivity above 90 K in a new Tl–Ba–Cu–O system, and pointed out that elemental substitutions in this system may lead to even higher-temperature superconductivity. Here we report stable and reproducible bulk superconductivity with an onset at 120 K and zero resistance above 100 K in the Tl–Ca/Ba–Cu–O system. This transition temperature is much higher than those observed for typical rare-earth-containing superconductors, and the onset temperatures are comparable to that in the Bi–Ca/Sr–Cu–O system, as reported in refs 10 and 11 (received after submission of this paper).

A typical procedure for preparing Tl–Ca/Ba–Cu–O samples is as follows. Appropriate amounts of Tl\(_2\)O\(_3\), CaO and Ba\(_2\)CuO\(_4\) for a certain nominal composition (for example, Tl\(_{1.7}\)Ca\(_{0.3}\)BaCu\(_{3}O\(_{8+x}\)\)), were completely mixed, ground and pressed into a pellet with a diameter of 7 mm and a thickness of 2–3 mm. The pellet was then put into a tube furnace, which had been heated to 880–910 °C, and was heated for 3–5 min in flowing oxygen. The sample was then taken from the furnace and quenched to room temperature in air. Some heated samples were furnace-cooled to room temperature, and some quenched samples were subsequently annealed at 450 °C for several hours. We use Ba\(_2\)CuO\(_4\) as a starting material because it has the lowest melting point among the Ba–Cu oxides, and molten Ba\(_2\)CuO\(_4\) is extremely fluid\(^9\); we believe that melt-solid reactions take place more completely than do typical solid-state reactions. The Ba\(_2\)CuO\(_4\) used in this experiment was prepared according to the procedure described in refs 8, 9 and 11.

Resistance was measured by the standard four-probe technique, with silver paste contacts. Rectangular bars of typical size 7 x 3 x 1 mm were cut from the pellets for resistance measurements. The resistance of the Tl–Ca/Ba–Cu–O samples usually starts to drop sharply at ~120 K, and reaches zero resistance above 100 K. The midpoint of the superconducting transition is ~110 K. We estimate the onset temperature as the temperature at which the curvature in the resistance versus temperature graph changes most rapidly\(^10\). In our data this is in agreement with the onset as determined by the intersection of the slopes in the transition region and in the normal region above the transition. Figure 1 shows resistance plotted versus temperature for a furnace-cooled Tl\(_{1.7}\)Ca\(_{0.3}\)BaCu\(_{3}O\(_{8+x}\)\) sample (open circles) and a Tl\(_{1.8}\)Ca\(_{0.2}\)BaCu\(_{3}O\(_{8+x}\)\) sample annealed at 450 °C (solid line). For comparison, Fig. 1 also shows the behaviour of a EuBa\(_2\)Cu\(_{3}O\(_{7-x}\)\) sample (dashed line) which was carefully prepared using a typical solid-state sintering technique. The transition midpoint and zero-resistance temperatures for the Tl\(_{1.8}\)Ca\(_{0.2}\)BaCu\(_{3}O\(_{8+x}\)\) sample are 112 and 103 K, which are the highest among the Tl–Ca/Ba–Cu–O samples prepared so far, and are much higher than those observed for high-quality rare-earth-containing samples (for example, refs 13 and 14), and the zero-resistance temperature is higher than those attained so far in the Bi–Sr/Ca–Cu–O system\(^10,11\). The superconducting transition of the Tl–Ca/Ba–Cu–O samples is rather broad (usually > 20 K), suggesting that zero resistance could be reached at higher temperatures with improvement of the preparation procedure.

Qualitative magnetic examinations of Tl–Ca/Ba–Cu–O samples showed strong diamagnetic repulsion. Figure 2 shows a sample with a nominal composition of Tl\(_{2}\)Ca\(_{3}\)BaCu\(_{5}O\(_{7+\delta}\) levitating over a magnetic field of ~5,000 G after immersion in liquid nitrogen.

Figure 2 A Tl–Ca/Ba–Cu–O sample levitating over a magnetic field of ~5,000 G after immersion in liquid nitrogen.

Figure 3 Temperature dependence of the a.c. susceptibility of a Tl\(_{1.8}\)Ca\(_{0.2}\)BaCu\(_{3}O\(_{7-x}\)\) sample.
Tl₂O₃ vapor process of making Ti-Ba-Ca-Cu-O superconductors

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A new process for making Ti-Ba-Ca-Cu-O superconductors which is based on reactions between solid precursor Ba-Ca-Cu-oxides and vapor Tl₂O₃ has been developed. The Tl₂O₃ vapor process allows Ti-Ba-Ca-Cu-O superconductors to be easily made in the forms of complex bulk components, wires and fibers, and thick and thin films, and minimizes problems caused by toxicity and volatility of Tl starting compounds.

Discovery of the Ti-Ba-Ca-Cu-O superconducting system has provided increased Tc with zero-resistance temperature up to 125 K. Structural and compositional analyses have shown that the Ti-Ba-Ca-Cu-O system can form a number of superconducting compounds, including Ti₆Ba₂CaₐCuₘOₙ₊₁ with m = 2 (Refs. 4–9) and 1 (Ref. 10) and n = 1–4 (Refs. 4–11). The Tc of these compounds increases with n as well as m. These trends have stimulated a strong search for higher Tc Ti-based superconductors by increasing n and/or m. For many applications, the Tc of a superconductor usually must be 1/2–1/4 higher than operating temperature. With the advantages of high Tc and easy formation, the Ti-Ba-Ca-Cu-O superconductors may be the first liquid-nitrogen temperature superconductors for practical commercial applications. However, the high toxicity and volatility of the Ti starting compounds have introduced safety concerns in the fabrication of Ti-based superconductors. In extensive preparation experiments on Ti-based superconductors, we have found that Tl₂O₃ evaporates above its 717°C melting point, and the vapor reacts with solid Ba-Ca-Cu-oxides, forming high quality Ti-Ba-Ca-Cu-O superconductors. This vapor-solid reaction has simplified the making of Ti-Ba-Ca-Cu-O superconductors to the making of Ba-Ca-Cu-oxides, and this minimizes the toxicity problem of Ti starting compounds. In particular, this Tl₂O₃ vapor process allows the Ti-Ba-Ca-Cu-O superconductors to be easily made in the forms of complex bulk components, wires and fibers, and thick and thin films by fabrication of the precursor Ba-Ca-Cu-oxides and subsequent introduction of Tl. This technique may also be of importance in understanding of the formation of Ti-Ba-Ca-Cu-O superconductors, and the search for new, even higher temperature, Ti-based superconductors.

Ba-Ca-Cu-oxides were first prepared using the method similar to that we previously developed for preparation of Ba-Cu-oxides. Appropriate amounts of BaCO₃, CaO (or CaCO₃), and CuO were mixed, ground, and heated at 925–950°C in air for 24–48 h with several intermediate grindings. The resulting uniform black material was ground and served as master material. An appropriate amount of the Ba-Ca-Cu-oxide powder was pressed into a pellet, and the pellet was heated at 925–950°C in flowing oxygen for 5–10 min and then was air cooled. A small platinum boat was put in a quartz boat, and a small amount of Tl₂O₃ (typically 0.1–0.2 g) was put into the platinum boat. The heated Ba-Ca-Cu-O pellet was put above the platinum boat. The quartz boat with the contents was put into a tube furnace, which had been heated to 900–925°C, and was heated for about 3 min in flowing oxygen followed by furnace cooling.

After the above heating treatment, the Tl₂O₃ in the platinum boat had completely evaporated, and the Tl₂O₃ vaporprocessed Ba-Ca-Cu-O pellet formed a layer of Ti-Ba-Ca-Cu-O superconducting compound(s) on its bottom surface. Figure 1 shows temperature dependences of resistance for some Tl₂O₃ vaporprocessed Ba-Ca-Cu-O precursors: (a) BaCa₂Cu₌O₇, (b) Ba₂CaCu₃O₇, and (c) Ba₂Ca₂Cu₄O₁₀. Their zero-resistance temperatures are 110, 96, and 105 K, respectively, which are comparable to those of corresponding sintered samples.

In principle, this technique has simplified the preparation of Ti-Ba-Ca-Cu-O to the preparation of Ba-Ca-Cu-O. Therefore, this technique allows Ti-Ba-Ca-Cu-O superconducting components, such as bulk components, wires and fibers, thick and thin films, to be easily made. In particular, Tl₂O₃ vaporprocessed molten Ba-Ca-Cu-oxides are also superconducting, and thus this technique allows superconducting components to be easily made in arbitrary shape. Figure 2 shows resistance-temperature dependences for (a) a Tl₂O₃ vaporprocessed Ba₂Ca₂Cu₃O₇ thick wire and for (b) a Tl₂O₃ vaporprocessed Ba₂Ca₂Cu₃O₇ thick film. The thick film was prepared by first melting Ba₂Ca₂Cu₃O₇ on a platinum substrate (heating at 980°C in flowing oxygen for 5 min) and then subjecting to Tl₂O₃ vapor processing. It reached zero resistance at 111 K. This 2-mm-wide film was...
Superconductivity in the Tl-Sr-Ca-Cu-O system

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Superconductivity at 20 K has been unambiguously observed in the Tl-Sr-Ca-Cu-O system. Superconductivity at 70 K was also observed in the same system. These observations may provide a new insight into the mechanism of oxide superconductivity.

Discoveries of Tl-based superconducting systems and Bi-based superconducting systems have not only set new and Bi-based superconducting systems have not only set new high-Tc records with zero resistance up to 125 K but also have provided a new insight into the mechanism of the new generation of rare-earth-free superconductors have shown that there are no Cu-O chains but Cu-O sheets are apparently responsible for superconductivity in these new systems, and thus Cu-O chains which were thought important in rare-earth-based 1:2:3 compounds are not required for cuprate superconductivity; (b) Tc increases with the number of Cu-O layers per unit cell, the Tl2Ba2Ca2Cu3O10+x having the highest Tc (zero resistance at 125 K) has three Cu-O layers; and (c) buckling of Cu-O sheets of superconducting compounds may lead to decrease of Tc (Refs. 12 and 14).

The existing experimental data also indicate that group-IIA elements are required for oxide superconductivity, playing perhaps a subtle role. Until now, Ba has been required for the Tl-based cuprate superconductors, whereas Sr is required for the Bi-based cuprate superconductors. At present, theorists are not able to predict whether superconductive compounds can be formed with substitution of Sr for Ba in the Tl-based cuprate superconducting systems, or substitution of Ba for Sr in the Bi-based cuprate superconducting systems. In extensive element substitutions for the Tl-based superconducting systems, we have observed 20-K superconductivity and possible 70-K superconductivity in the Tl-Sr-Ca-Cu-O system. The samples are stable and the results are reproducible. The discovery of the Tl-Sr-Ca-Cu-O superconducting system bridges the Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O superconductors, and should provide further clues to an understanding of the mechanism of high Tc oxide superconductivity.

A typical procedure of preparing Tl-Sr-Ca-Cu-O superconducting samples is the following. Appropriate amounts of Tl2O3 (99.999% pure), SrO (99.5% pure), CaO (99.95% pure), and CuO (certificate reagent) were mixed and ground completely to obtain a powder with certain nominal compositions (for example, Tl2Sr2Ca2Cu3O10+2). The powder was pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was then put into a tube furnace which had been heated to 900-950°C, and was heated for 3-5 min in flowing oxygen, followed by furnace cooling or quenching. Since a small amount (<1%) of barium entering into the Tl-Sr-Ca-Cu-O system could lead to observation of superconductivity above liquid-nitrogen temperature, great care was paid in avoiding contamination with barium. Qualitative chemical analyses were performed for samples 1 and 2 (both with a nominal composition of Tl2Sr2Ca2Cu3O10+2) using a JSM model 35 scanning electron microscope, operated at 20 kV and 0.01 μA beam current. The major elements in both samples were Tl, Sr, Ca, and Cu. Sample 1, in addition, contains a trace (<2%) of Ag, perhaps from silver paste or from capsule contamination. Neither sample contains detectable barium (<1%).

Electronic behavior of the Tl-Sr-Ca-Cu-O samples is strongly dependent on both the starting composition and the preparation conditions. Above liquid-nitrogen temperature, three patterns of temperature dependence of resistance were observed: semiconductive, semiconductive-metallic, and metallic. Most nominal Tl2Sr2Ca2Cu3O10+2 samples prepared using the above procedure showed a metallic-like temperature dependence of the resistance above liquid-nitrogen temperature. Two of these samples (1 and 2, which were prepared by heating at 900°C for 3 min followed by furnace cooling to 700°C and by heating at 950°C for 3 min followed by quenching to room temperature, respectively) were investigated down to liquid-helium temperature by four-probe resistance, dc SQUID magnetization, and the field derivative of the microwave absorption, dH/dH, at 9.2 GHz (Ref. 18). The same investigations were also carried out for an additional sample (3) with a nominal composition of Tl2SrCa2Cu3O9+x, which was prepared by heating at...
RESISTANCE FLUCTUATIONS IN THE Y-Ba-Cu-O-F SYSTEM

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Abstract

Two batches of samples with nominal composition of \( \text{YBa}_2\text{Cu}_3\text{O}_{6.5-x}\text{F}_x \) (\( x=0-2 \)) were prepared. All fluorine-containing samples were multiphase. Resistance-temperature relationships of these samples depended strongly on their fluorine content and their preparation conditions. Resistance-temperature anomalies were observed for some samples with large values of \( x \). Combining transport measurements with x-ray powder diffraction data, we attribute these anomalies either to existence of high temperature superconductive phase(s) in the Y-Ba-Cu-O-F system, or to resistance fluctuations resulting from the presence of multiple phases.

After the discovery of 90 K superconductors in Y-Ba-Cu-O system (1), superconductors with even higher transition temperatures have been actively sought. Trace superconductivity at 240 K was reported in Y-Ba-Cu-O system...
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-IIIB 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 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 even in a system which contains no rare-earth elements. The samples are stable in air at ambient temperature for at least two months (according to resistance 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 TlO3, 99.999%-pure BaCO3, 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 RBa2Cu3O7-x superconductors are used, is as follows: Appropriate amounts of BaCO3 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, BaCu304). The powder was then placed in a quartz boat containing the pellet was then put into a tube furnace, which had been heated to 880-9 K. 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...
Bulk superconductivity at 120 K in the Tl–Ca/Ba–Cu–O system

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The discovery of 30-K superconductivity in the La–Ba–Cu–O system and 90-K superconductivity in the Y–Ba–Cu–O system stimulated a worldwide search for even higher-temperature superconductors. Unfortunately, most of the higher-temperature transitions reported in the past year have proved to be unstable, irreproducible, or not due to bulk superconductivity. Recently, we and co-workers reported superconductivity above 90 K in a new Tl–Ba–Cu–O system, and pointed out that elemental substitutions in this system may lead to even higher-temperature superconductivity. Here we report stable and reproducible bulk superconductivity with an onset at 120 K and zero resistance above 100 K in the Tl–Ca/Ba–Cu–O system. This transition temperature is much higher than those observed for typical rare-earth-containing superconductors, and the onset temperatures are comparable to that in the Bi–Ca/Sr–Cu–O system, as reported in refs 10 and 11 (received after submission of this paper).

A typical procedure for preparing Tl–Ca/Ba–Cu–O samples is as follows. Appropriate amounts of Tl₂O₃, CaO and BaCu₂O₄ for a certain nominal composition (for example, Tl₃CaBaCu₄O₁₁), were completely mixed, ground and pressed into a pellet with a diameter of 7 mm and a thickness of 2–3 mm. The pellet was then put into a tube furnace, which had been heated to 880–910 °C, and was heated for 3–5 min in flowing oxygen. The sample was then taken from the furnace and quenched to room temperature in air. Some quenched samples were subsequently annealed at 450 °C in flowing oxygen for several hours. We use BaCu₂O₄ as a starting material because it has the lowest melting point among the Ba–Cu oxides, and molten BaCu₂O₄ is extremely fluid; we believe that melt-solid reactions take place more completely than do typical solid-state reactions. The BaCu₂O₄ used in this experiment was prepared as described in refs 8, 9 and 11.

Resistance was measured by the standard four-probe technique, with silver paste contacts. Rectangular bars of typical size 7 × 3 × 1 mm were cut from the pellets for resistance measurements. The resistance of the Tl–Ca/Ba–Cu–O samples usually starts to drop sharply at ~120 K, and reaches zero resistance above ~100 K. The midpoint of the superconducting transition is ~110 K. We estimate the onset temperature as the temperature at which the curvature in the resistance versus temperature changes most rapidly. In our data this is in approximate agreement with the onset as determined by the intersection of the slopes in the transition region and in the normal region above the transition. Figure 1 shows resistance plotted as a function of temperature for a furnace-cooled Tl₃Ca₁₅BaCu₄O₈₊ₓ sample (open circles) and a Tl₅CaBaCu₄O₁₁ sample annealed at 450 °C (solid line). For comparison, Fig. 1 also shows the behaviour of a EuBa₂Cu₃O₇–ₓ sample (dashed line) which was carefully prepared using a typical solid-state sintering technique. The transition midpoint and zero-resistance temperatures for the Tl₃Ca₁₅BaCu₄O₈₊ₓ sample are 110 K and 103 K, which are the highest among the Tl–Ca/Ba–Cu–O samples prepared so far, and are much higher than those observed for high-quality rare-earth-containing samples (for example, refs 13 and 14), and the zero-resistance temperature is higher than those attained so far in the Bi–Sr/Ca–Cu–O system.10,11

The superconducting transition of the Tl–Ca/Ba–Cu–O samples is rather broad (usually >20 K), suggesting that the zero resistance could be reached at higher temperatures. Improvement of the preparation procedure resulted in a marked increase in the onset temperature of the superconducting transition, which is much higher than those observed for high-quality rare-earth-containing samples (for example, refs 13 and 14), and the zero-resistance temperature is higher than those attained so far in the Bi–Sr/Ca–Cu–O system.10,11

Qualitative magnetic examinations of Tl–Ca/Ba–Cu–O samples showed strong diamagnetic repulsion. Figure 2 shows the magnetic susceptibility of a Tl₃Ca₁₅BaCu₄O₁₁ sample levitating over a magnetic field of ~5,000 G after immersion in liquid nitrogen. Figure 3 shows the temperature dependence of the a.c. susceptibility of a sample of nominal composition Tl₅Ca₁₅BaCu₄O₁₁, as determined by the technique of Norton and Maxwell. The onset temperature as determined by the deviation in the slope of the diamagnetic susceptibility curve indicates a superconducting transition temperature of ~120 K.
We have discovered a reproducible and stable bulk superconductor above 90 K with zero resistance at 81 K in the Ti-Ba-Cu-O system. By appropriate elemental substitutions in this system, we have observed reproducible and stable bulk superconductivity in the Ti-Ca-Ba-Cu-O system above 120 K, which is much higher than that observed for any existing rare earth-containing superconductor. The Ti-Ca-Ba-Cu-O superconductor samples are easily made and readily levitate over a magnetic field. We believe that further elemental substitutions in the thallium-containing systems may produce even higher temperature superconductors.

1 Introduction

Discoveries of 30 K superconductivity in the La-Ba-Cu-O system [1] and 90 K superconductivity in the Y-Ba-Cu-O system [2] have stimulated a worldwide race for higher temperature superconductors. In spite of many efforts in the past year, stable and reproducible superconductivity has remained at the level of 90 K in the RE(rare earth)-Ba-Cu-O system. Breakthroughs were recently made by the discoveries of the 90 K Ti-Ba-Cu-O system [3,4], 110 K Bi-Ca-Sr-Cu-O system [5,6] and 120 K Ti-La-Ba-Cu-O system [7,8]. The Ti-Ba-Cu-O system is the first non-rare-earth system which reaches zero resistance above liquid nitrogen temperature, whereas the Ti-Ca-Ba-Cu-O system is the first system which reaches zero resistance above 100 K, and has the highest zero-resistance temperature (125 K). In this paper, we present the preparation procedures and properties of the new Ti-based superconductors, and briefly discuss further exploration for even higher temperature superconductors.

2. The 90 K Ti-Ba-Cu-O Superconductor

Samples were prepared using 99.999 % pure Ti2O3, 99.999 % pure BaCO3, and certificate reagent CuO. Since Ti2O3 has a relatively low melting point of 717 °C and starts to decompose at a temperature as low as 100 °C, typical procedures used for preparing REBa2Cu3O7-x superconductors do not apply to the Ti-Ba-Cu-O system. In our preparation of the Ti-Ba-Cu-O superconductor, we used short high temperature heating and quenching. High temperature is required for
Magnetization of the 120-K Tl-Ca-Ba-Cu-O superconductor

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dc magnetization measurements on the new Tl-Ca-Ba-Cu-O superconductor show superconductivity with an onset temperature as high as 118 K, 24 K higher than that of a high-quality Eu-Ba2Cu3O7-δ sample. The resistive onsets of these new superconductors are near 140 K. The magnetic data show complete diamagnetic flux exclusion and 10-15% Meissner expulsion at 10 K.

Discoveries of 30-K superconductivity in the La-Ba-Cu-O system\(^1\) and 90-K superconductivity in the Y-Ba-Cu-O system\(^2\) have stimulated a worldwide race for higher-temperature superconductors. In spite of many efforts in the past year, stable and reproducible superconductivity has remained at the level of 90 K in the R-Ba-Cu-O system (\(R\) equals rare earth). Breakthroughs were recently made in rare-earth-free superconductors by the discoveries of the 90-K Tl-Ba-Cu-O system,\(^3,4\) 110-K Bi-Ca-Sr-Cu-O system,\(^5,6\) and 120-K Tl-Ca-Ba-Cu-O system.\(^7-9\) The Tl-Ca-Ba-Cu-O superconducting samples have onset and zero-resistance temperatures much higher than those of the Bi-Ca-Sr-Cu-O system.\(^7,9\) Two superconducting phases have been identified.\(^9\) One has a composition of Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{10+x}\), (2:2:2:3 phase), and another of Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{11+x}\), (2:1:2:2 phase, which is similar to Bi\(_2\)Ca\(_2\)Sr\(_2\)Cu\(_2\)O\(_{8+\delta}\)). In this Brief Report we report magnetization and resistance data on the Tl-Ca-Ba-Cu-O samples. The onset temperature of magnetization is 117-118 K, 23 K higher than that of a high-quality Eu-Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) sample.

Two samples with nominal compositions Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{9+\delta}\), and Tl\(_2\)Ca\(_4\)Ba\(_4\)Cu\(_3\)O\(_{11+\delta}\), used in the present experiments were prepared using Tl\(_2\)O\(_3\), CaO, and BaCu\(_3\)O\(_4\) in the same batch.\(^6\) Both were heated at 900 °C for 3 min and furnace cooled. The resistance-temperature dependences of these two samples are shown in Fig. 1. The resistance was measured by the standard four-probe technique with silver-paste contacts. These two samples both have onset temperatures near 140 K (defined by the smallest curvature of the resistance-temperature curve\(^10\)), midpoint of 127 K, and zero-resistance temperature at 121 K. Zero-resistance data correspond to resistivities less than \(10^{-6}\) \(\Omega\) cm. The difference of calcium contents in these two samples does not seem to have significantly changed their superconducting behavior, which depends strongly on preparation conditions of the samples. Note that the Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{9+\delta}\) sample consists of approximately 80% of the new 2:2:2:3 superconducting phase.\(^9\)

Magnetization measurements were performed utilizing a superconducting quantum interference device (SQUID) magnetometer manufactured by BTI Corp., San Diego, CA. Figures 2 and 3 show dc magnetization (field cooled and zero field cooled) as a function of temperature for an applied field of 1 mT for samples of Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{10+x}\), and Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{11+x}\), respectively, whose resistive behavior is shown in Fig. 1. The Meissner flux expulsion is 10-15% of the diamagnetic flux exclusion; the magnitude of the diamagnetic shielding is large and consistent with complete flux exclusion from the samples at 10 K. This behavior is similar to that observed in Tl-Ba-Cu-O,\(^4\) La-Ba(Sr)-Cu-O,\(^11\) and Y-Ba-Cu-O samples.\(^12\) Explanations suggested to date include existence of a superconducting glass state,\(^11\) anisotropy effects,\(^13\) and superconductivity confined to thick shells around normal grains.\(^12\) At this stage, we hesitate to speculate on differentiation between these causes, and only note that our samples were

![FIG. 1. Resistance-temperature dependences of samples Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{9+\delta}\) (triangles) and Tl\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_3\)O\(_{11+\delta}\) (circles).](image-url)
New 120 K Ti-Ca-Ba-Cu-O superconductor


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Electronic and magnetic properties of the new 120 K Ti-Ca-Ba-Cu-O superconductor are presented. Resistance-temperature variations, ac susceptibility, and the (low) magnetic field dependence of the critical current density are reported. The new superconductor can be prepared in a molten state, which should allow processing leading to high critical current density. Preliminary x-ray diffraction data are also presented.

Discoveries of 30 K superconductivity in the La-Ba-Cu-O system and 90 K superconductivity in the Y-Ba-Cu-O system have stimulated a worldwide race for higher temperature superconductors. In spite of much effort in the past year, stable and reproducible superconductivity has remained at the level of 90 K in the RE (rare earth)-Ba-Cu-O system. Breakthroughs were recently made by the discoveries of the 90 K Ti-Ba-Cu-O system, 110 K Bi-Ca-Sr-Cu-O system, and 120 K Ti-Ca-Ba-Cu-O system. 7 In this letter, we report electronic and magnetic data on the new superconducting Ti-Ca-Ba-Cu-O system, and present preliminary critical current density data and x-ray diffraction patterns of the new generation of high-temperature superconductors in comparison with those of the conventional RE-Ba-Cu-O systems.

Ti-Ca-Ba-Cu-O samples used in the present experiments were prepared using the procedure similar to that we previously described. 7 Briefly, appropriate amounts of TiO, CaO, and BaCuO (or Ba,CuO) were completely mixed and ground, and pressed into a pellet. The pellet was then put into a tube furnace, which had been heated to 880-920 °C, and was heated for 3-5 min in flowing oxygen. The sample was then furnace cooled to room temperature in about 1 h. The BaCuO and Ba,CuO were prepared according to the procedure we previously developed.8 A series of samples with nominal compositions of Ti,Ca,BaCuO with y = 1, 1.5, 2, 3, and 4 was prepared. Samples with nominal composition of Ti,Ca,BaCuO were also synthesized. All samples readily levitate over a magnetic field. Because our samples are multiphase, the strong Meissner effect observed is due to both a large volume fraction of superconductive phase and to a higher transition temperature. Furnace cooling slightly improves the superconducting behavior of the samples. This indicates that the Ti-Ca-Ba-Cu-O superconducting compound is stable over a relatively large range of temperatures, and thus the Ti-Ca-Ba-Cu-O superconductor may be of importance in many applications. We believe that annealing in oxygen is not required for these samples and that the improvement of the superconducting behavior is mainly due to the decrease in damage to the crystalline structure by slow cooling.

Resistance was measured by the standard four-probe technique with silver paste contacts. Figure 1 shows resistance-temperature dependence for a sample with y = 4. The zero-resistance temperature of this sample is 106 K, three degrees higher than that which we reported previously for a sample with y = 1.5 (see Ref. 7). Usually, the onset temperature of the sharp drop in resistance, defined by smallest curvature of resistance-temperature curve, 9 is above 120 K, and we believe that a higher temperature for zero resistance could be achieved by improvement of preparation procedure. 19

Figure 2 shows 5 kHz ac susceptibility for a sample with y = 4 as measured by the technique of Norton. 11 The onset temperature of susceptibility drop of this sample is about 117 K (as seen in the high gain inset), and the lower temperature leveling occurs at about 85 K.

The Ti-Ca-Ba-Cu-O superconductor can be prepared in a molten state at a relatively low temperature (900-950 °C), and this preparation only slightly suppresses the transition temperature (and does not destroy superconductivity). Figure 3 shows the resistance-temperature dependence of a sample with nominal composition of Ti,Ca,Ba,CuO and of a sample prepared from the molten material with the same nominal composition. This makes this superconductor

![Figure 1. Resistance-temperature dependence of a Ti,Ca,Ba,CuO sample.](image-url)
AKRONI-PENNEY BAND STRUCTURES FOR ONE DIMENSIONAL SUPERLATTICES

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ABSTRACT

Detailed calculations of high order band-gap boundaries are given as functions of potential barrier heights and widths for a range of superlattice structures. Prominent features of the structures include a multitude of band-gaps above the barrier as well as many band crossings. An interpretation of the crossings provides an approximate formula for estimating the band structure.

1. INTRODUCTION

The advent of molecular beam epitaxy and plasma enhanced chemical vapor deposition has resulted in the fabrication of high quality crystalline and amorphous multilayer superlattice structures. The potential energy distribution of these structures has been modeled by an infinite number of periodic square wells (Kronig-Penney model) perpendicular to the superlattice layers (Figure 1). Experiments in photon absorption, carrier transport and resistivity have been performed on these structures with the results strongly supporting the Kronig-Penney model.

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A Melt-Processible High Temperature Superconductor

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Abstract

We report the preparation and characterization of a melt-processible high-temperature superconductor based on a melt reaction between YBa$_2$Cu$_3$O$_{7-x}$ and Y$_{1.2}$Ba$_{0.6}$Cu$_3$O$_{y}$ at 950°C. The samples have sharp superconducting transitions above 90K as determined by resistivity and AC susceptibility measurements. X-ray diffraction shows crystal structures nearly identical to those of YBa$_2$Cu$_3$O$_{7-x}$ sintered superconductors. The dense void-free melt-processible superconductors have potential for large single crystal growth and for high critical currents with low-cost processing.
Melt-processible rare earth-Ba-Cu-O superconductors based on molten Ba-Cu oxides

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Ba-Cu oxides with certain compositions were found to be meltable or partly meltable at a relatively low temperature of 950 °C. High-quality, dense, and void-free high-temperature superconductors based on rare earth (RE)-Ba-Cu oxides of the form REBa2Cu3Ox have been made by reactions between molten Ba-Cu oxides and solid RE-containing materials at the same temperature. This has allowed superconductive components to be made in a wide variety of shapes. This melt process will significantly alter oxide superconductor preparation procedures, and will allow growth of large single crystals aiding in the understanding of the mechanism of superconductivity and in the search for superconductivity at even higher transition temperatures.

The discovery of 35 K superconductivity in the La-Ba-Cu-O system by Bednorz and Muller1 was soon followed by the finding of 90 K superconductivity in the Y-Ba-Cu-O system.2 The superconductive compound YBa2Cu3O7+x was rapidly identified,3 and a series of REBa2Cu3O7+x superconductors, with RE = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu, was prepared with a similar transition temperature.4 This breakthrough of above-liquid-nitrogen temperature superconductivity has simulated strong activity in theoretical and experimental research aimed at finding superconductivity at even higher transition temperatures, up to or even above room temperature.

Superconductors of the type REBa2Cu3O7+x are conventionally prepared as ceramics by solid-state reactions, and useful forms are fabricated by compression. The ceramic materials are porous, and the preparation process is relatively intractable for manufacturability. In a series of experiments on substitution of rare earths for Y in YBa2Cu3O7+x, we found that TbBa2Cu3O7+x melts (partly) at 950 °C—a typical temperature at which other rare earth-barium-copper oxides form sintered superconductors by solid-state reaction, and that the molten TbBa2Cu3O7+x reacts with Y1.2Ba0.8CuO3.6+x to form a high-quality superconductor.5 In this letter we report a new finding, that Ba-Cu oxides with certain compositions are meltable or partly meltable at 950 °C, and that the molten Ba-Cu oxides react with RE-containing materials, such as RE oxides, RE-Ba- and RE-Cu-binary oxides, or RE-Ba-Cu-ternary oxides, to form melt-processible high-quality, dense, and void-free superconductors of the REBa2Cu3O7+x class. This finding has allowed high-quality superconductor components of arbitrary shape to be fabricated at a relatively low temperature. We believe the melt process will significantly alter the superconductor sample preparation procedures used by researchers in this field, and is ultimately expected to be of importance in the understanding of the mechanism of high-temperature oxide superconductivity, and in the search for new superconductors with even higher transition temperatures.

A typical procedure for preparing this kind of melt-processible superconductor is as follows: appropriate amounts of BaCO3 and CuO were mixed and ground in an agate mortar, and heated in air at 900 °C for 12 h to obtain a material with nominal composition of Ba2CuO3. The heated mixture was reground and pressed into a pellet. Similarly, Y2O3, BaCO3, and CuO were mixed, ground, and heated in air at 950 °C for 12 h to obtain the material with nominal composition of Y1.2Ba0.8CuO3.6+x. The heated mixture was powdered. The Ba2CuO3 pellet was put on the Y1.2Ba0.8CuO3.6+x powder, heated in flowing O2 at 950 °C for 24 h in a tube furnace, and then at 650 °C for 4 h.

Finally, the materials were furnace cooled in flowing O2 to less than 200 °C in 1–2 h after they were removed from the furnace. After the heating at 950 °C, the gray-black Ba2CuO3 pellet has partly melted. A black melt-recrystallized-like superconductive chunk (usually a half-sphere with a diameter, for example, about 1 cm) was formed, which was embedded in excess dark-green Y1.2Ba0.8CuO3.6+x powder. The Y1.2Ba0.8CuO3.6+x powder was then removed. Rectangular parallelepiped samples were cut with a saw to typical dimensions of 1×2×7 mm.

Several samples were prepared from interior cuts of the original half-sphere.

The x-ray powder diffraction pattern of this melt-processible material was the same as that of YBa2Cu3O6.5–x with two additional lines [at d = 2.52 Å (111) and 2.33 Å (111)] characteristic of a small amount of CuO present. This melt-processible material has a density of about 6.4 g/cm3, close to the value of 6.3 g/cm3 for YBa2Cu3O6.5–x predicted from theory.6 This material could be easily levitated in a magnetic field, and showed a strong diamagnetic flux exclusion above liquid-nitrogen temperature, comparable to that of any sample we have carefully prepared using the conventional sinter method.7 This sample had a midpoint transition temperature of 93 K and a transition width of about 2 K, as measured by a standard four-probe method.8 Figure 1 shows a typical variation of resistance as a function of temperature down to liquid-nitrogen temperature.

According to Cava et al.,3 the Y1.2Ba0.8CuO3.6+x consists of 1/3 of black superconductive phase YBa2Cu3O5.5+x, and 2/3 of nonsuperconductive green phase Y1.2BaCuO3. In the above example, formation of the high-quality black...
Microstructural Analysis of Y-Ba-Cu-O Superconductors by Light Microscopy

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The room temperature microstructure of sintered Y-Ba-Cu-O superconductors as determined by light microscopy is reported in this paper. The sintered superconductors contain porosity in a platelet matrix of superconductor phase. The platelet growth habit suggests liquid-phase sintering is a dominant mechanism for growth.

INTRODUCTION

Microstructural analysis using light microscopy has been a powerful tool for quantifying features such as grain size, grain shape, phase size, and phase shape in metallic systems. In ceramic based systems, the use of light microscopy has been limited to materials that are capable of reflecting light. Struers Inc. (1) have shown that light microscopy can be used to investigate the configuration of silicon wafers, determine the integrity of the interface bond between alumina and a metallic coating, and estimate the