

phys. stat. sol. (a) 158, 179 (1996)

Subject classification: 74.72; 61.66; S10.15

Structural Research Laboratory (a) and Department of Applied Chemistry (b),
University of Science and Technology of China, Hefei¹⁾,
Department of Physics, University of Arkansas, Fayetteville²⁾ (c), and
Department of Geology, University of New Mexico, Albuquerque³⁾ (d)

Phase and Superconductivity of (Tl,M)-Sr-Cu-O System (M = Cr or V)

Experimental Evidence for Possible Existence of Sr-Based Tl-2212-Phase

By

Z. Y. CHEN (a, b), H. M. LUO (b), Z. Z. SHENG (c), B. QU (b),
Y. T. QIAN (a, b), and L. M. WANG (d)

(Received June 20, 1996)

Tl-M-Sr-Cu-O (M = Cr or V) samples were prepared from ultrafine Cu powder and Tl₂CO₃, and studied by TEM, ED, and XRD. The results indicate that the samples consist mainly of 1201 phase and a small amount of a tetragonal phase with larger cell parameters $a = 0.39$ nm and $c = 3.0$ nm. This phase is believed to be Sr-based 2212 phase, which is related to the superconductivity at liquid nitrogen temperature.

1. Introduction

It is well known that Ca-free TlSr₂CuO_z with orthorhombic structure is easy to form [1]. By its composition, the Sr-based 1201-type compound is similar to superconducting TlBa₂CuO_z, but its resistivity only decreases with decreasing temperature and exhibits metallic behavior. It is not superconducting in spite of improved preparation conditions. However, interestingly, by partially substituting Cr or V for Tl, nominal (Tl,M)Sr₂CuO_z (M = Cr or V) samples exhibit a two-step superconducting transition at 40 to 50 K and near liquid nitrogen temperature [2, 3]. It is imaginable that the phase responsible for the former superconductivity is the Sr-based analog of TlBa₂CuO₅ (1201 phase), and the phase for the latter is the Sr-based 1212 phase or another phase like a Ba-based superconducting phase, because T_c of only the 1212-type phase, for example, TlSr₂CaCu₂O₇ [4] and TlSr₂(Sr_{0.5}R_{0.5})Cu₂O_z (R = rare earth elements) [5 to 7] is near or above liquid nitrogen temperature. Previously, in our work [3], the X-ray diffraction patterns of nominal (Tl,M)Sr₂CuO_z (M = Cr or V) samples were indexed with the tetragonal 1201-type indices, but some peaks could not be indexed well and the superconductivity at liquid nitrogen temperature was not explained reasonably. The unindexed peaks may be related to the superconductivity at liquid nitrogen temperature. In this paper, we report

¹⁾ Anhui, Hefei 230026, People's Republic of China.

²⁾ Fayetteville, Arkansas 72701, USA.

³⁾ Albuquerque, NM 87131, USA.

**EFFECTS OF V- OR Cr-DOPING ON
PHASE FORMATION, ELECTRIC PROPERTIES AND
SUPERCONDUCTIVITY OF THE
3212-TYPE PHASE $\text{Pb}_2\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_3\text{O}_z$**

Z. Y. CHEN and Y. T. Qian

*Structural Research Laboratory, University of Science & Technology of China (USTC),
Academia Sinica, Hefei, 230026, China*

Department of Applied Chemistry, USTC, Hefei, 230026, China

H. M. LUO and B. QU

Department of Applied Chemistry, USTC, Hefei, 230026, China

Z. Z. SHENG

Department of Physics, University of Arkansas, Fayetteville, AR72701, USA

L. M. WANG

Department of Geology, University of New Mexico, Albuquerque, NM87131, USA

Received 24 January 1996

Revised 24 May 1996

The effects of vanadium or chromium on the formation, electric properties and superconductivity of Pb-3212 phase $(\text{Pb}_2\text{Cu})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_z$ are studied. The sites of V or Cr in $\text{PbO}-\text{CuO}_5-\text{PbO}$ structure unit for Pb-3212 phase is also investigated. Compared with the effects of Cr-doping, V can totally substitute Ca to form a new compound $\text{Pb}_2\text{Sr}_2(\text{V}_{0.5}\text{Y}_{0.5})\text{Cu}_3\text{O}_z$, and V has relatively greater substitution amount in $(\text{Pb}_{2-x}\text{M}_x)\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_3\text{O}_z$ ($\text{M} = \text{Cr}$ or V). Moreover, the resistivity and superconductivity of the above samples decrease with increasing V or Cr amount. Among them, the effects of V is greater, and its location (in Pb or Ca site) also affects greatly the superconductivity.

1. Introduction

Since the first superconducting lead cuprates, $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}$ (3212 phase, $(\text{Pb}_2\text{Cu})\text{Sr}_2\text{YCu}_2\text{O}_{8+\delta}$), were discovered by Cava *et al.*,¹ a variety of new lead cuprates including 1201, 1212, 1222, 2212, 2222, 3201, 3212 and 3222 phases have been synthesized.^{2,3} However, it is not always easy to obtain the Pb-3212 and Pb-3222 samples exhibiting good, reproducible superconducting properties because

A new (Hg, V)-based 1212-type cuprate (Hg, V) $\text{Sr}_2(\text{Y}, \text{Ca}) \text{Cu}_2\text{O}_z$ with $T_{c(\text{onset})}$ up to 110 K

O. Chmaissem, Z.Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received: 22 November 1994 / Revised version: 21 February 1995

Abstract. We have successfully synthesized a new (Hg, V)-based 1212-type cuprate $(\text{Hg}_{1-x}\text{V}_x) \text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_z$. The electrical resistance measurements showed that some of the as-synthesized materials with proper Hg/V and Y/Ca ratios exhibit weak superconductivity. Oxygen-annealing significantly improved their superconducting behavior, and $T_{c(\text{onset})}$ up to 110 K was observed. The lattice parameters of (Hg, V)-1212 were found to be in the order of $a = 3.8415(1) \text{ \AA}$ and $c = 11.8514(6) \text{ \AA}$. Substituting mercury atoms by vanadium ones results in an important increase of the a parameter and an important decrease of the c parameter compared to the known Hg-based Sr-bearing compounds. The crystal structure of (Hg, V)-1212 was refined by Rietveld refinement against X-ray powder data using the tetragonal symmetry of space group $P4/mmm$. The V and Cu valence states and superconductivity in this new (Hg, V)-1212 cuprate are briefly discussed.

PACS: 74.70-b; 74.70.Vy; 74.60.Mj

Introduction

Following the discovery of 94-K superconductivity in $\text{HgBa}_2\text{CuO}_{4+\delta}$ [1] and the observation of 133.5-K superconductivity in the Hg-Ba-Ca-Cu-O system [2], an intensive effort was given by an important number of researchers, and many new superconducting Hg-based materials were synthesized, including the 1212-type Hg-based Sr-containing compounds $(\text{Hg}, M) \text{Sr}_2(\text{Ca}, R) \text{Cu}_2\text{O}_{6+\delta}$, where M and R stand for metallic ion and rare-earth, respectively. The followings are some of them: $(\text{Hg}_{1-x}\text{M}_x)\text{Ba}_2(\text{Y}_{0.6}\text{Ca}_{0.4}) \text{Cu}_2\text{O}_{6+\delta}$ ($M = \text{Ca} + \text{Cu}$) [3], $(\text{Hg}_{1-x}\text{Cu}_x)\text{Ba}_2(\text{Nd}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_{6+\delta}$ [4], $(\text{Hg}_{0.5}\text{Tl}_{0.5})\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_{6+\delta}$ [5], $(\text{Hg}_{0.4}\text{Pr}_{0.6})\text{Sr}_2(\text{Sr}_{1-y}\text{Pr}_y)\text{Cu}_2\text{O}_{6+\delta}$ [6], and $(\text{Hg}_{1-x}\text{Bi}_x)\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_{6+\delta}$ [7–9].

The Hg-based family is structurally analogous to the Tl-based family with TlO mono-layer. According to our

experience with the 1212-type, especially, Tl-based cuprate superconductors (see for example, [10]), where chemical substitutions result in new compounds with even higher T_c , we believe that many new Hg-based compounds using this technique will be synthesized, and higher T_c 's may be achievable with the right elements of substitution. As effective substitution elements, Cr, V, and Mo have the special capability to form superconducting cuprates and to enhance T_c [11–14]. Single elemental substitution in the Tl-based Sr-bearing 1212 cuprate may enhance T_c to above 100 K (see, for example, [11]). It is reasonable to surmise that similar Hg-based 1212-type cuprates substituted with these elements could also form and might exhibit higher T_c . We recently successfully synthesized and characterized a new (Hg, Cr)-based 1212-type cuprate $(\text{Hg}, \text{Cr}) \text{Sr}_2(\text{Y}, \text{Ca}) \text{Cu}_2\text{O}_{6+\delta}$ [15], in which, however, superconductivity was not clearly detected. We were also successful in the synthesis of (Hg, V)-based 1212 cuprate $(\text{Hg}, \text{V}) \text{Sr}_2(\text{Y}, \text{Ca}) \text{Cu}_2\text{O}_{6+\delta}$. This cuprate exhibits $T_{c(\text{onset})}$ up to 110 K. To the best of our knowledge, this $T_{c(\text{onset})}$ is the highest one ever reported for a (Hg, M)-based Sr-containing 1212-type superconductor. We report herein on the synthesis, electrical measurements, and structure refinement of this new (Hg, V)-based 1212-type cuprate $(\text{Hg}, \text{V}) \text{Sr}_2(\text{Y}, \text{Ca}) \text{Cu}_2\text{O}_{6+\delta}$, and discuss briefly the valence states of Cu and V and the superconductivity in this new cuprate.

Experimental

Samples with nominal compositions $(\text{Hg}_{1-x}\text{V}_x)\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_z$ were synthesized by a two-step solid state reaction method. Precursors $\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y) \text{Cu}_2\text{O}_z$ were first prepared using high purity powders of $\text{Sr}(\text{NO}_3)_2$, Y_2O_3 , CaO and CuO as starting materials. Appropriate amounts of chemicals were mixed in an agate mortar and fired in a preheated furnace at 750°C under flowing gas of oxygen until the strontium nitrates were completely decomposed (about 3 h). Then, the temperature was gradually raised to $900\text{--}920^\circ\text{C}$ and the sample was maintained at this temperature for about 18 hours before being pulled



ELSEVIER

Physica C 242 (1995) 23–29

PHYSICA C

New 1212-type (Hg, Cr)-based cuprate (Hg_{1-x}Cr_x)Sr₂(Ca_{1-y}Y_y)Cu₂O_{6+δ}

O. Chmaissem, Z.Z. Sheng *

Department of Physics, and High Density Electronics Center, University of Arkansas, Fayetteville, AR 72701, USA

Received 17 June 1994; revised manuscript received 3 October 1994

Abstract

We have successfully synthesized a new 1212-type (Hg, Cr)-based cuprate (Hg_{1-x}Cr_x)Sr₂(Ca_{1-y}Y_y)Cu₂O_{6+δ} (0.1 ≤ x ≤ 0.5 and 0.1 ≤ y ≤ 0.5). According to X-ray diffraction data, the samples with x ≥ 0.2 and y ≤ 0.2 are 90–95% pure 1212 phase. The structure of the (Hg, Cr)-1212 compound is tetragonal of space group P4/mmm. Depending on the nominal composition, the lattice parameters are in the order of a = 3.8526 Å and c = 11.8194 Å. Refinements of the structure show the presence of two extra oxygen atoms O(3) and O(4) in the (Hg, Cr) layer at the position (½, ½, 0) and (½, 0, 0), respectively. The (Hg, Cr)-1212 samples are not superconducting, and show a semiconducting behavior instead. The non-superconductivity of the samples is explained in terms of the concept of mixed Cu²⁺/Cu³⁺ valence.

1. Introduction

Putilin et al. [1] reported on March 1993 the discovery of a new mercury-based superconductor HgBa₂CuO_{4+δ} with T_{c onset} up to 94 K, the highest ever observed in a 1201-type cuprate superconductor. This was the first member of the homologous series Hg-Ba₂Ca_{n-1}Cu_nO_{2n+2+δ} with T_{c onset} as high as 134 K observed later by Schilling et al. [2]. Since then, intensive work has been carried out on the new mercury family and many new phases have been isolated. In the 1212-type structure, several compounds have been found so far, for example: (Hg_{1-x}M_x)Ba₂(Y_{0.6}Ca_{0.4})Cu₂)_{6+δ} (M = Ca + Cu) [3], (Hg_{1-x}Cu_x)Ba₂(Nd_{1-y}Ca_y)Cu₂O_{6+δ} [4], (Hg_{0.5}Tl_{0.5})Sr₂(Y_{1-y}Ca_y)Cu₂O_{6+δ} [5], (Hg_{0.4}Pr_{0.6})Sr₂(Sr_{1-y}Pr_y)Cu₂O_{6+δ} [6], and (Hg_{1-x}Bi_x)Sr₂(Y_{1-y}Ca_y)Cu₂O_{6+δ} [7–9].

The Hg-based family is structurally analogous to

the Tl-based family with TlO monolayer. According to our experience with the Tl-based cuprate superconductors, where chemical substitutions result in new compounds with even higher T_c, we believe that many new Hg-based compounds will be synthesized using this technique, and higher T_c's may be achievable with the right elements of substitution. Also, in the course of searching for new mercury superconductors, it is obvious that non-superconducting compounds may be first obtained, such as Hg-Ba₂RCu₂O_{6+δ} (R = Rare Earth), as reported earlier by Putilin et al. [10].

Chromium as an effective element of substitution was first used in the Tl–Sr–Ca–Cu–O system [11,12]. A large enhancement of T_c was observed in the 1201-type compound (Tl, Cr)Sr₂CuO₅ (40–250 K, a T_c of 77 K was also observed), and the 1212-type compound (Tl, Cr)Sr₂(Ca, Cr)Cu₂O₇ (110 K). Recently, Shimoyama et al. [13] reported the synthesis of a new 1201-type (Hg, Cr)-based superconductor (Hg_{1-x}Cr_x)Sr₂CuO_{4+δ} (58 K, for x = 0.3). We stud-

* Corresponding author.



ELSEVIER

Physica C 247 (1995) 125-132

PHYSICA C

Electrical properties and crystal structure of (Hg, Pb)Sr₂(Ca, Y)Cu₂O_{6+δ}

O. Chmaissem, Z.Z. Sheng *

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 19 October 1994; revised manuscript received 28 March 1995

Abstract

The (Hg, Pb) based 1212-type cuprate (Hg, Pb)Sr₂(Ca, Y)Cu₂O_{6+δ} with $T_{c\text{ onset}}$ up to 100 K was synthesized. The effect of O annealing on T_c was studied. Rietveld refinements of the structure were carried out with a tetragonal structure of space group P4/mmm. A local disorder was observed in the (Hg, Pb)O_δ layers. Better refinement results were obtained using models in which (Hg, Pb) atoms and O(3) atoms are shifted off their ideal positions from (0, 0, 0) to (x, 0, 0) or (x, x, 0) and from ($\frac{1}{2}$, $\frac{1}{2}$, 0) to (x', $\frac{1}{2}$, 0) or (x', x', 0), respectively. The refined composition is (Hg_{0.651}Pb_{0.300}Cu_{0.049})Sr₂(Y_{0.264}Ca_{0.616}Hg_{0.120})Cu₂O_{6.84}. According to the mixed valence concept of Cu^{2+/3+} and Pb^{2+/4+}, Pb is most likely at 4+ valence.

1. Introduction

The discovery of superconductivity in the mercury-based materials HgBa₂Ca_{n-1}Cu_nO_{4n+2+δ} with T_c 's as high as 135 K [1,2] was immediately followed by the synthesis of an important number of new Hg bearing compounds. The T_c of 135 K and the results with T_c up to 164 K under high pressure [3,4] gave some hope that T_c can still go higher. A lot of attention has been given to the barium-containing mercury-based system Hg-Ba-Ca-Cu-O which is studied in detail. Many papers reported on the synthesis, superconducting properties, characterization, and structural determination of the different member of this series. The valences of Hg, Ba, and Ca of 2+, 2+, and 2+ makes it easy to determine

the copper valence based only on the amount of the extra oxygen atoms O(δ) located in the mercury layer. A simple equation, $\nu_{\text{Cu}} = 2 + 2\delta/n$, gives the average valence of copper in the different members of the series HgBa₂Ca_{n-1}Cu_nO_{4n+2+δ}.

On the other hand, (Hg, M)Sr₂(Ca, R)Cu₂O_{6+δ} (M = metallic element; R = rare earth) had received less attention probably because of their T_c 's which are generally lower than those of their analogues in the Hg-Ba-Ca-Cu-O system. The structure and electrical properties of (Hg, M)Sr₂(Ca, R)Cu₂O_{6+δ} still need to be studied in more details.

As part of our continuing efforts to understand the physical and chemical properties of high- T_c oxide superconductors, the (Hg, Pb)Sr₂(Ca, Y)Cu₂O_{6+δ} compound was chosen to be the object of a detailed synthesis, characterization, and structural study. The 1212-type cuprate (Hg, Pb)Sr₂(Ca, Y)Cu₂O_{6+δ} was first synthesized by Hu et al. [5], who found that

* Corresponding author.



ELSEVIER

Physica C 248 (1995) 42-48

PHYSICA C

Crystal structure and T_c of 1212-type cuprate (Tl,Cr)Sr₂(Ca,Tl)Cu₂O₇

Y.F. Li, O. Chmaissem, Z.Z. Sheng *

Physics Department, University of Arkansas, Fayetteville, AR 72701, USA

Received 2 November 1994; revised 24 February 1995

Abstract

The crystal structure of the 1212-type cuprate (Tl,Cr)Sr₂(Ca,Tl)Cu₂O₇ was investigated using X-ray diffraction data and the Rietveld refinement technique. The refinement was performed using the tetragonal symmetry of space group P4/mmm. It was found that Cr atoms entered the Tl site while partial Tl atoms occupied the Ca site. (Tl,Cr) atoms displaced from the origin to (0.101(1), 0, 0), and O(3) shifted from (0.5, 0.5, 0) to (0.626(8), 0.5, 0). The refined lattice parameters were $a = 3.8155(1)$ Å and $c = 12.0222(5)$ Å. The refined composition was (Tl_{0.812}Cr_{0.100}Ca_{0.088})Sr₂(Ca_{0.842}Tl_{0.158})Cu₂O₇. Cr atoms were most likely to be at a high valence state. The enhancement of T_c in the (Tl,Cr)-1212 cuprate is briefly discussed based on the structure parameters by comparison with the un-doped TlSr₂CaCu₂O₇.

1. Introduction

Soon after the discovery of the 125 K TlBaCaCuO system [1], the TlSrCaCuO system was also found to be superconducting [2]. There are two homologous series of Tl-based superconductors: double-(TlO)₂-layer Tl₂Ba₂Ca_{n-1}Cu_nO_{2n+4} and single-TlO-layer TlBa₂(or Sr₂)Ca_{n-1}Cu_nO_{2n+3} [3-7]. The latter is called 1212 phase when $n = 2$, for both Ba and Sr versions. Unlike its counterpart TlBa₂CaCu₂O₇, however, TlSr₂CaCu₂O₇ is hard to prepare in the pure form [2,8-10]. It has been proved that doping with other elements can improve the situation significantly. For example, Pb-doped TlSrCaCuO forms 1212 phase (Tl,Pb)Sr₂CaCu₂O₇ with T_c up to 85 K [10-13] and rare earth(R)-doped TlSrCaCuO forms 1212 phase TlSr₂(Ca,R)Cu₂O₇ with T_c of 90 K

[14-16]. Moreover, double substitution of Pb for Tl and R for Ca may improve T_c up to 105 K [16,17]. It was found that doping with V, Cr or Mo can also effectively promote the formation of 1212 phase and improve T_c [18-20]. Single Cr, V, or Mo doping may improve T_c to above 100 K. The Cr-doped TlSr₂CaCu₂O₇ exhibits T_c as high as 110 K [18]. In addition, V- or Cr-doped 1201 and 1223 type compounds were also synthesized [21-26]. Therefore, there is a new series of Tl-based superconducting compounds (Tl,D)(Sr,Ba)₂Ca_{n-1}Cu_nO_{2n+3} with D = d-element, which may be of importance in practical applications (see Refs. [23] and [27], for example). Although the previous work (X-ray diffraction) showed the dominant existence of superconducting phases, the detailed crystal structures remained to be determined. We recently conducted Rietveld refinement based on X-ray diffraction for the Cr-doped 1212-type compound (Tl,Cr)Sr₂CaCu₂O₇. In this pa-

* Corresponding author.

Enhancement of $T_{c \text{ onset}}$ in $(\text{Ga,Hg})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$ by Hg doping

O. Chmaissem, Z.Z. Sheng *

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 7 October 1994; revised manuscript received 28 November 1994

Abstract

We synthesized a new 1212-type cuprate $(\text{Ga}_{1-x}\text{Hg}_x)\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y)\text{Cu}_2\text{O}_7$. Partial substitution of divalent Hg for trivalent Ga simplifies the synthesis conditions of the 1212 compound and enhances its $T_{c \text{ onset}}$ up to 88 K. Similar to $\text{GaSr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$, its structure is orthorhombic of space group $\text{Ima}2$. The lattice parameters are in the order of $6a_p \times b_p \sqrt{2} \times c_p \sqrt{2}$, (p refers to a primitive perovskite). No phase transition (orthorhombic \rightarrow tetragonal; large unit cell \rightarrow reduced unit cell) was observed when varying the ratios Ga:Hg and/or Y:Ca.

1. Introduction

The Ga based 1212-type cuprate, $\text{GaSr}_2\text{YCu}_2\text{O}_7$, was first reported by Roth et al. [1] and by Vaughney et al. [2]. This cuprate becomes superconducting when the Y site is doped by Ca. $\text{GaSr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ with $x=0.2$ exhibits a T_c in the order of 30 K [2]. Increasing the amount of calcium up to 0.8 results in an important increase of $T_{c \text{ onset}}$ up to 70 K [3]. A unique feature of this cuprate is that gallium atoms are tetrahedrally coordinated by oxygen, i.e. the M-O_6 octahedra seen in the Tl based and Hg based cuprates are replaced by Ga-O_4 tetrahedra. The Ga based 1212 compound is found to crystallize in the orthorhombic symmetry of space group $\text{Ima}2$ [1,2]. The lattice parameters are in the order of $6a_p \times b_p \sqrt{2} \times c_p \sqrt{2}$, where a_p , b_p , and c_p are the unit-cell parameters of a primitive perovskite. This doubled unit cell (with respect to those of Tl based and Hg based 1212-type compounds) is due to the tendency of the gallium–oxygen planes to be ar-

ranged in a non-centrosymmetrical fashion within one unit cell.

The synthesis procedures of the superconducting $\text{GaSr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_x$ reported by the different groups were somewhat complicated and time consuming. Heating periods as long as three weeks followed by high-pressure annealing (200–300 atm) in pure oxygen for about 24 h were necessary for the obtention of the desired phase, as reported by Dabrowski et al. [3], for example. A recent report by Isobe et al. [4] seems to be simplifying the synthesis procedures with heating the nominal sample first at 950°C for 3 days, second at 1000°C (in oxygen) for another 3 days, and finally heating in oxygen at temperatures in the order of 1000–1100°C for an additional 3 days. However, the highest $T_{c \text{ onset}}$ reported so far is around 70 K.

In this paper, we report on the synthesis of a new (Ga,Hg) based 1212-type cuprate $(\text{Ga}_{1-x}\text{Hg}_x)\text{Sr}_2(\text{Y}_{1-y}\text{Ca}_y)\text{Cu}_2\text{O}_7$ (using the sealed quartz tube technique) and the enhancement of its $T_{c \text{ onset}}$ up to 88 K as the result of doping with mercury. Powder X-ray diffraction showed that the new (Ga,Hg) based 1212-type cuprate adopts the same

* Corresponding author.

Flux pinning and motion of high- J_c Tl(2223) Ag-sheathed tapes

Yuping Sun, Faipei Zhang, Jianyi Jiang, Anming Hu, and Jiaju Du
Institute of Solid State Physics, Academia Sinica, Hefei 230031, People's Republic of China
and Structure Research Laboratory, University of Science and Technology of China, Hefei 230026,
People's Republic of China

Yuheng Zhang
Structure Research Laboratory, University of Science and Technology of China, Hefei 230026,
People's Republic of China

Z. Z. Sheng
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 19 August 1994; accepted for publication 7 November 1994)

The dependence of resistance on temperature has been measured for a Tl-system 2223-phase Ag-sheathed tape with J_c ($J_c = 1.5 \times 10^4$ A/cm², 77 K, 0 T) in an applied magnetic-field range from 0 to 0.8 T. The experimental results can be explained in terms of the thermally activated flux creep model. The relationship between pinning potential U_0 and the applied magnetic field H oriented parallel to and perpendicular to the tape surface is, respectively, $U_{0\parallel} = 0.12H^{-0.22}$ eV and $U_{0\perp} = 0.065H^{-0.35}$ eV. The relationship between pinning potential U and T follows: $U(T, H) = U_0(H)(1 - t)$ ($t = T/T_0$, $T_0 \approx 141$ K). When H and the measuring current I are laid in the same tape surface, the broadened resistive transition is independent of the configuration between H and I , namely, an energy dissipation is independent of a macroscopic Lorentz force. The phenomenon is accounted for according to the two-dimensional pancakelike vortex-antivortex model based on the characteristic of a stronger intrinsic plane pinning of layer superconductors. © 1995 American Institute of Physics.

I. INTRODUCTION

The flux line will move due to the action of thermal activation and Lorentz force when the high- T_c superconductor (HTSC) lies in mixed state; so, it will cause energy loss, namely, dissipation. This property is similar to a traditional low- T_c superconductor (LTSC); however, the T_c of HTSC is so high that the flux motion of HTSC is more serious than that of the LTSC: It experiences the so-called "giant flux creep."¹ On the other hand, the very short coherence length and the high anisotropy of the HTSC result in the complexity of the flux pinning and the motion of the HTSC. The dissipation owing to the flux motion seriously restricts the capability of carrying a large current of the HTSC in a magnetic field. In order to make the HTSC have more practical applications within the liquid-nitrogen temperature (LNT) range it is necessary to study the flux pinning and motion of the HTSC. So far, the Bi-system 2212 single crystal and film and Y-system single crystal and film²⁻⁴ have been investigated. Recently Hu *et al.*⁵ have studied the Bi-system 2223-phase Ag-clad tape. For the Tl-system superconductor, because of the easy evaporation and the toxicity of Tl, others only fundamentally studied a bulk material.⁶ Few people have fully explored the Tl-system composite tape.

We have prepared high- J_c ($J_c = 1.5 \times 10^4$ A/cm², 77 K, 0 T) Tl-system 2223-phase Ag-clad tape by the powder-in-tube method. The grains in the tape have better c -axis preferred orientation.

We have measured the broadened resistive transitions in the magnetic fields and explained the experimental results in terms of the thermally activated flux creep model and given the pinning potential within the magnetic-field range from 0 to 0.8 T. The dissipation for the H and the I lying in the same tape surface and the H parallel to the I has been discussed.

II. EXPERIMENTAL TECHNIQUES

First, the Tl-Ba-Ca-Cu-O 2223-phase bulk materials were prepared by the method of solid-state reaction,⁷ then the bulks were pulverized. The thin tapes with thickness from 0.12 to 0.14 mm were prepared by the powder-in-tube method described in Ref. 8. The x-ray pattern of the tape after the surface Ag was removed and the scanning electron microscopy (SEM) fracture image of the tape shows that the grains in the tape are of definite c -axis preferred orientation.

The resistance measurements were carried out by means of the four-probe method. The size of the sample was $25 \times 3 \times 0.12$ mm³. The temperature range from 10 to 300 K was obtained by means of cryogenic refrigeration equipment. The magnetic fields from 0 to 1 T were provided by a magnet.

When the contact resistance between the surface Ag and the superconducting grains was not considered, the measured resistance value was the composite resistance of the Ag and the superconductor, so the resistance value of the superconductor is equal to that with the surface Ag resistance taken out of the measured resistance value.

III. RESULTS AND DISCUSSION

Figure 1 shows the curves of the broadened resistive transitions when the superconducting tape was laid in different magnetic fields. Figure 1(a) shows that the fields H are parallel to the tape surface and perpendicular to the current-measuring I . Figure 1(b) shows that the fields are perpendicular to the tape surface. Figure 1 shows that the resistive transitions become broader with the increase of the fields. Meanwhile, it also manifests that the broadened resistive transitions of the Tl-system 2223-phase tape are of stronger anisotropy. The broadened resistive transitions for the $H \perp$ tape surface are more obvious than those for the $H \parallel$ tape

**RAPID SYNTHESIS OF NEARLY-PURE HIGH T_c SUPERCONDUCTOR
 $\text{HgBa}_2\text{CuO}_{4+x}$ AT AMBIENT PRESSURE IN AN OPEN SYSTEM**

Z.Z.Sheng, Y.F.Li, and D.O.Pederson

Department of Physics, and University of Arkansas, Fayetteville, AR 72701, USA

(Received 28 November 1994; accepted 27 March 1995 by R.C. Dynes)

Nearly-pure 1201-type cuprate $\text{HgBa}_2\text{CuO}_{4+x}$ was successfully synthesized at ambient pressure in an open system, and was characterized by powder x-ray diffraction analyses and by resistance and ac susceptibility measurements. The lattice parameters are $a = 3.8742(5)$ Å and $c = 9.4798(11)$ Å, and the $T_{c,\text{onset}}$ is up to 95 K. The results of the present experiment are instructive to the understanding of the formation mechanism of Hg-based superconductors, and thus to the preparation of existing Hg-based superconductors and to the search for new Hg-based high T_c superconductors.

Keywords: A. high- T_c superconductors, B. chemical synthesis.

The discovery of 94-K $\text{HgBa}_2\text{CuO}_{4+x}$ (ref. 1) has led to a new family of Hg-based superconductors including the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ (ref. 2) which are isostructural to the mono-TlO-layer superconductors $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ (ref. 3). Since the Hg-based superconductors exhibit higher T_c up to 135 K, and under very high pressures, up to about 160 K^{4,5}, they have attracted much attention of superconductor community. However, the preparation of these new materials is very delicate because the decomposition of HgO at low temperature (500 °C). Until this date, the superconducting Hg-based samples were prepared, without exception, under pressure in a sealed container (for example, in a sealed quartz tube)^{1,2,4-12}. In this communication, we reported that Hg-1201 phase can form at ambient pressure, and that we have successfully prepared superconducting $\text{HgBa}_2\text{CuO}_4$ samples with even nearly pure Hg-1201 phase in an open system.

Soon after the Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O high- T_c superconducting systems were discovered¹³⁻¹⁶, in order to explore new and even higher T_c superconductors, we carried out extensive elemental substitutions for the Tl-based systems. Among them are elemental addition experiments of Zn, Cd, or Hg into the Tl-Ba-Cu-O system¹⁷. In the Hg-added Tl-Ba-Cu-O samples, we observed 85-K zero-resistance temperature and 95-K onset-temperature which were higher than those reported for any un-added Tl-Ba-Cu-O samples. We thus concluded¹⁷ that "Hg-addition can slightly increase T_c of the samples by 3-5 K if a proper preparation procedure is used." Since only preliminary powder x-ray diffraction analyses were carried out for the samples, the details of structure and composition of the 95-K superconducting phase in the Hg-added Tl-Ba-Cu-O samples remained to identify. The discovery of the Hg-based superconductors, led us to surmise that the

phase responsible for the 95-K superconductivity in our Hg-added Tl-Ba-Cu-O samples is just the Hg-1201 phase. However, all the Hg-Ba-Cu-O samples were prepared in a closed system as mentioned above, whereas our Hg-added Tl-Ba-Cu-O samples were prepared in an open system (i.e. in flowing oxygen or in air). Therefore, the key question is whether or not the Hg-1201 phase can form in an open system. For answering this question, we carried out extensive tests, and demonstrated that Hg-1201 phase, even nearly pure Hg-1201 phase, do form at ambient pressure in an open system. This result not only confirms that the 95-K superconductivity which we observed in the Hg-added Tl-Ba-Cu-O system¹⁷ originates from Hg-1201 phase, but also is instructive to the understanding of the formation mechanism of Hg-based superconductors, and thus to the preparation of existing Hg-based superconductors and to the search for new Hg-based high T_c superconductors.

Hg-Ba-Cu-O samples were prepared using a two-step procedure similar to that of ref. 17. In a typical procedure, a precursor with nominal composition of Ba_2CuO_3 was first prepared with $\text{Ba}(\text{NO}_3)_2$ (or BaO_2) and CuO by heating at 850 °C for 8-12 hours in flowing oxygen, and the precursor was then mixed with about the same weight of HgO, ground (in a dry box), and pelletized. The nominal $\text{HgBa}_2\text{CuO}_4$ pellet was put in a quartz tube (with an end sealed), quickly introduced into a preheated (800 - 900 °C) tube furnace (in a hood) with or without flowing O_2 , and heated for 45-90 seconds, followed by quickly pulling the quartz tube out of the furnace and cooled in air to room temperature. The samples were stored in a small bottle for protecting from moisture, and were then subjected to resistance, ac susceptibility, and powder x-ray diffraction measurements, as soon as possible. Resistance was measured by

Fabrication of Ag-clad (Tl, V)(Sr, Ba)₂Ca₂Cu₃O_y superconducting tapes

Y F Li†, Z Z Sheng†, Z F Ren†, J H Wang‡ and K C Gorett§

† Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

‡ Superconductive Materials Laboratory, State University of New York, Buffalo, NY 14214, USA

§ Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

Received 5 December 1994

Abstract. Ag-clad (Tl, V)(Sr, Ba)₂Ca₂Cu₃O_y tapes were fabricated by a powder-in-tube process. The tapes exhibited no discernible favourable texture. Critical current density (J_c) values at 77 K were $< 2000 \text{ A cm}^{-2}$ and were strongly influenced by heat treatment temperature and time. Pressing before the final annealing reduced the tape thickness and increased the J_c .

1. Introduction

Since the discovery of high-temperature superconducting oxides by Bednorz and Müller [1], many attempts have been made to fabricate wires or tapes from these oxides. Among the attempted fabrication techniques, powder-in-tube methods have become widely used because they are simple, effective, and easily scaled to production of long lengths [2-16].

Tl-based 1223 superconductors are often selected as the core material for tape production because of their attractive high critical temperature (T_c) and critical current density (J_c) and relatively high irreversible magnetic field [5, 8-11, 14-18]. Recently, we successfully synthesized V-doped TlSr₂Ca₂Cu₃O_y [19], in which the V was substituted on the Tl site. When compared with undoped TlSr₂Ca₂Cu₃O_y [20], T_c is raised from 94 to 105 K and the irreversibility line is substantially increased [21]. We also found that with a small amount of Ba substituting for Sr, phase formation became much easier and T_c was raised to $\approx 110 \text{ K}$ [22].

As-synthesized (Tl, V)(Sr, Ba)₂Ca₂Cu₃O_y grains have tended to be plate-like, often with lengths $> 50 \mu\text{m}$ and aspect ratios > 10 [21]. Such grains are of interest because they may allow favourable alignment during mechanical processing. To date, powder-in-tube wires and tapes made from Tl-based superconductors have exhibited relatively little favourable texture [3, 9, 10, 14-16]. V-doping of Tl-based superconductors also alters liquid-phase formation. (Formation of large plate-like grains is one consequence of the presence of a persistent liquid during synthesis.) Transient liquids have proved to be useful in the synthesis and sintering of high- T_c superconductors [16, 20, 23]. The goals of this work were to determine whether favourable texture could be induced by drawing and rolling a tube filled

with Tl_{0.5}V_{0.5}Sr_{1.75}Ba_{0.25}Ca₂Cu₃O_z ((Tl, V)-1223) powder and whether a sintering schedule could be found that would promote strong linkage of the superconductor grains. In this paper, we report some of our results.

2. Experimental methods

(Tl, V)-1223 was made by a two-step procedure. First, the nominal precursor Sr_{1.75}Ba_{0.25}Ca₂Cu₃O_z was synthesized by mixing SrO, BaO₂, CaO and CuO, and sintering the resultant powder at 870 °C for 72 h in flowing O₂, with intermittent grinding every 24 h. Tl₂O₃ and V₂O₃ was then mixed into the precursor. To compensate for Tl₂O volatilization, 25% excess Tl₂O₃ was added to the mixture. The powder was pressed into a pellet, placed in a loosely covered Al₂O₃ crucible, fired at 970 °C for 6 h in flowing O₂, and then cooled slowly to room temperature. The as-prepared material was nearly pure 1223 phase with $T_c = 110 \text{ K}$ [22].

The (Tl, V)-1223 pellet was crushed into a powder, which was loaded by vibration and ramming into closed-end, 6.35 mm outer diameter, 4.35 mm inner diameter Ag tubes. To drive out moisture, the filled tubes were heated at 700 °C in flowing O₂ for 4 h, after which the temperature was reduced to $\approx 120 \text{ °C}$ and the tubes were removed from the furnace. Each tube was quickly capped and sealed by Ag soldering. A standard power-in-tube procedure was used to fabricate flat tapes [15, 16]: the tubes were drawn into wires at ≈ 10 -15% reduction of diameter per pass; final diameters were 1-2 mm. After drawing, most of the wires were flat rolled into tapes of various final thickness [16]. After rolling, some tapes were pressed at $\approx 1 \text{ GPa}$.

Samples 3 cm long were cut from the tapes, capped with Ag foil to minimize loss of Tl, and heat treated.

Synthesis and characterization of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1, 2, \text{ and } 3$)

O. Chmaissem, L. Wessels, Z.Z. Sheng *

Department of Physics, and High Density Electronics Center, University of Arkansas, Fayetteville, AR 72701, USA

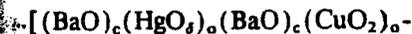
Received 17 May 1994; revised manuscript received 20 June 1994

Abstract

We have successfully prepared the first three members of the mercury-based superconducting compounds $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$, namely Hg-1201, Hg-1212 and Hg-1223 with high purity and very good quality. The influence of the synthesis parameters is studied in detail. Using the sealed quartz tube method, very simple procedures are found to ensure a 100% reproducibility of nearly 100% pure Hg-1201 and 85-90% Hg-1212 and Hg-1223. Oxygen annealing of the sample Hg-1201 at 300 °C for 18 h results in an enhancement of its critical temperature up to 97 K. The symmetry of the first and second members is tetragonal with lattice parameters $a = 3.8831(1) \text{ \AA}$, $c = 9.5357(2) \text{ \AA}$, and $a = 3.8624(1) \text{ \AA}$, $c = 12.7045(2) \text{ \AA}$, respectively. X-ray diffraction lines of Hg-1223 can be indexed in a tetragonal cell with $a = 3.8564(1) \text{ \AA}$ and $c = 15.8564(9) \text{ \AA}$ as well as in an orthorhombic cell with lattice parameters $a = 5.4537(1) \text{ \AA}$, $b = 5.4247(1) \text{ \AA}$, and $c = 15.8505(7) \text{ \AA}$.

1. Introduction

Following the discovery of superconductivity with $T_c = 94 \text{ K}$ in the one-layer $\text{HgBa}_2\text{CuO}_{4+\delta}$ compound [1], a variety of new mercury cuprates have been synthesized [2-10]. $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201) is the first member of the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$. The $T_{c \text{ onset}}$ of the first, second and third members are 94 K, 127 K and 134 K, respectively. $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ are isostructural to the Tl based superconductors $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ [11,12] but unlike the thallium compounds the mercury layers are heavily oxygen deficient. The structure of the Hg based superconductors $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ can be described as a sequence of layers:



in which blocks $(\text{BaO})_c(\text{HgO}_\delta)_o(\text{BaO})_c$ having the rock-salt structure and a thickness of about 5.5 Å alternate with blocks $(\text{CuO}_2)_o\{(n-1)(\text{Ca})_c(\text{CuO}_2)_o\}$ having a perovskite-like structure and an approximate thickness $[4.00 + (n-1) \times 3.16] \text{ \AA}$. The subscripts o and c indicate if the cation is at the origin or at the center of the mesh in each layer. All Hg-1201 [13,14], Hg-1212 [3] and Hg-1223 [15] are found to crystallize with symmetry of space group $P4/mmm$. An orthorhombic symmetry was also proposed by Meng et al. [16] for Hg-1223.

The research conducted on the thallium-based compounds showed that these materials offer a wide variety of possible substitutions on the different sites of their structures. Many compounds were prepared having their T_c above 100 K. As we mentioned above many new mercury-related compounds were already successfully synthesized with T_c around 100 K. Fur-

* Corresponding author.



ELSEVIER

Physica C 228 (1994) 190-194

PHYSICA C

Synthesis and characterization of (Hg, Bi)-based 1212-type cuprate superconductor $(\text{Hg}_{0.67}\text{Bi}_{0.33})\text{Sr}_2(\text{Y}_{0.67}\text{Ca}_{0.33})\text{Cu}_2\text{O}_{6+\delta}$ ($\delta = 0.68$)

O. Chmaissem, L. Wessels, Z.Z. Sheng *

Department of Physics and High Density Electronics Center, University of Arkansas, Fayetteville, AR 72701, USA

Received 28 April 1994; revised manuscript received 16 May 1994

Abstract

(Hg, Bi)-based 1212-type compound $(\text{Hg}_{0.67}\text{Bi}_{0.33})\text{Sr}_2(\text{Y}_{0.67(1)}\text{Ca}_{0.33(1)})\text{Cu}_2\text{O}_{6+\delta}$ was synthesized by using the sealed quartz tube method. The $T_{c(\text{onset})}$ based on resistance and AC susceptibility measurements was up to 100 K. Rietveld refinements of the structure of (Hg, Bi)-1212 were carried out in the tetragonal symmetry with space group $P4/mmm$. The lattice parameters are $a = 3.80960(8)$ Å and $c = 12.0157(4)$ Å. The refined Y:Ca ratio is 0.67(1):0.33(1) while the refined occupancy factor of the oxygen atoms located in the (Hg, Bi)-layer is 0.68(2). The results in the present experiment are explained based on the concept of mixed Cu valencies.

1. Introduction

The discovery of the Hg-1201 cuprate superconductor $\text{HgBa}_2\text{CuO}_{4+\delta}$ [1] was immediately followed by the synthesis of the Hg-1212 and Hg-1223 [2-4]. Similar to Tl-based superconductors, there exists a whole series of Hg-based compounds with the general formula $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$. The Hg-based compounds have a tetragonal structure and crystallize with the space group symmetry of $P4/mmm$. Samples of Hg-1223 with orthorhombic symmetry were also synthesized [5,6]. The critical temperatures of Hg-1201, Hg-1212 and Hg-1223 are 94, 127 and 135 K, respectively. High pressure experiments showed T_c up to 157 K for Hg-1223 samples [7,8], which suggested that chemical substitutions could replace the effect of the high pressure and might result in higher T_c at ambient pressure.

Chemical substitutions are very effective for the synthesis of new cuprate superconductors. According to the concept of average Cu valence, the 1212-type cuprates may be written as $(\text{B}, \text{S}_1)(\text{A}, \text{S}_2)_2(\text{A}', \text{S}_3)\text{Cu}_2\text{O}_{6+x}$, where B, A, and A' are metallic atoms and S_1 , S_2 , and S_3 are substitutes [9]. Obviously, the discovery of the new Hg-based superconductors will certainly lead to various new Hg-based superconductors. Several substituted Hg-based compounds including substituted Hg-based 1212 compounds have been reported, for example, $(\text{Hg}_{1-x}\text{M}_x)\text{Ba}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{6+\delta}$ ($\text{M} = \text{Ca} + \text{Cu}$) (90 K) [10], $(\text{Hg}_{1-x}\text{Cu}_x)\text{Ba}_2(\text{Nd}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{6+y}$ (110 K) [11], $(\text{Hg}_{0.5}\text{Tl}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{6+\delta}$ [12], and $(\text{Hg}_{0.4}\text{Pr}_{0.6})\text{Sr}_2(\text{Sr}_{1-x}\text{Pr}_x)\text{Cu}_2\text{O}_{6+\delta}$ (85 K) [13] were reported.

Pelloquin et al. [14] reported the synthesis of $(\text{Hg}_{0.5}\text{Bi}_{0.5})\text{Sr}_2(\text{R}_x\text{Ca}_{1-x})\text{Cu}_2\text{O}_{6+\delta}$ ($\text{R} = \text{Nd}, \text{Y}$). The sample with $\text{R} = \text{Nd}$ exhibits $T_{c(\text{onset})}$ up to 94 K ($\text{R} = \text{Nd}$). The samples prepared with $\text{R} = \text{Y}$ and

* Corresponding author.

Synthesis and properties of $Tl_{0.6}V_{0.5}Sr_2Ca_2Cu_3O_x$

Y.F. Li^a, Z.Z. Sheng^a, S. Sengupta^{b,1}, K.C. Goretta^{b,*}, P.E.D. Morgan^c

^a Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

^b Argonne National Laboratory, Argonne, IL 60439, USA

^c Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, CA 91360, USA

Received 8 July 1994

Abstract

Powder of approximate composition $Tl_{0.6}V_{0.5}Sr_2Ca_2Cu_3O_x$ was synthesized in O_2 at $970^\circ C$ from a mixture of oxides of nominal composition $Tl_2V_{0.5}Sr_2Ca_2Cu_3O_x$. The onset T_c was 110 K. Magnetic hysteresis measurements indicated that above ≈ 60 K the irreversibility behavior was superior to that of $TlBa_2Ca_2Cu_3O_x$, which has a T_c of ≈ 118 K. The individual grains were up to $\approx 50 \mu m$ in length, with aspect ratios < 10 , which may during fabrication promote texturing by mechanical means.

1. Introduction

Although Tl based superconductors with one Tl–O layer exhibit better flux pinning than their two-Tl-layer counterparts, their irreversibility behaviors remain inferior to that of $YBa_2Cu_3O_x$ [1–4]. Alloying can affect the irreversibility [3] and many elements have been substituted successfully into Tl superconductors. For example, there are wide ranges of solution between Ba and Sr, and between Tl and Pb, Bi, or Cr [2–11]. These substitutions have caused T_c to decrease slightly, but in the case of $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$, improvements in irreversibility [3] over $TlBa_2Ca_2Cu_3O_x$ [1,12,13] have been reported.

We have recently synthesized a family of (Tl, V)(Sr, Ba) $_2$ Ca $_2$ Cu $_3$ O $_x$ (V doped 1223) superconductors [14,15]. Zero-resistance values were 100–110 K, with Ba additions raising T_c slightly. The work re-

ported here includes details of new synthesis efforts for these V doped materials, microstructural characterization, and magnetic measurements of J_c and irreversibility. Data are compared with those for pure $TlSr_2Ca_2Cu_3O_x$ [5,6] and $TlBa_2Ca_2Cu_3O_x$ [12,13,16].

2. Experiments

Tl_2O_3 , V_2O_3 , and $Sr_2Ca_2Cu_3O_x$ powders with nominal composition $Tl_2V_{0.5}Sr_2Ca_2Cu_3O_x$ were mixed in an agate mortar [14]. The resultant powder was pressed into pellets 12 mm in diameter and 2 mm thick. The pellets were placed into covered Al_2O_3 crucibles, heated for 5 h at $970^\circ C$ in flowing O_2 , and cooled slowly to room temperature. During heating substantial Tl was lost from the pellets.

For comparison with the V doped 1223, $TlSr_2Ca_2Cu_3O_x$ (Sr-1223) and $TlBa_2Ca_2Cu_3O_x$ (Ba-1223) powders were synthesized and characterized. The Sr-1223 was prepared from $Sr_2Ca_2Cu_3O_x$ mixed with Tl_2O_3 . The powders were fired in air at $750^\circ C$

* Corresponding author.

¹ Present address: Superconductive Components Inc., 1145 Chesapeake Ave., Columbus, OH 43212, USA.

Rev. **18**, 145 (1956).
 ndoven 1959.
5, 441 (1961).
 and K. SAHL, IEEE Trans. Magnetics
 Fine Interactions **28**, 487 (1986).
 magnetic Mater. **62**, 57 (1986).
 y, to be communicated.
 a) **14**, 485 (1966).
 ad 1991.
 d State **20**, 1661 (1978).
 d State **17**, 202 (1975).
 , 859 (1977).
 State Chem. **37**, 144 (1981).

Solid State **4**, 749 (1964).
 85).
 3).
 V. R. MARATHE, V. S. DHARSHANE
 (1985).

(Received June 3, 1991)

phys. stat. sol. (a) **142**, 459 (1994)

Subject classification: 74.70; S10.15

*Institute of Solid State Physics, Academia Sinica, Hefei¹ (a),
 Department of Physics, University of Arkansas, Fayetteville² (b), and
 Structure Research Laboratory, University of Science and Technology of China, Hefei³*

Preparation and Properties of High J_c Tl(2223) Ag-Sheathed Tape

By

YUPING SUN (a), FAIPEI ZHANG (a), JIANYI JIANG (a), ANMING HU (a),
 YINFONG WANG (a), JIAJU DU (a), Z. Z. SHENG (b), and YUHENG ZHANG (c)

The techniques of preparation of silver-sheathed tape of the Tl-Ba-Ca-Cu-O superconductor with high J_c ($= 1.5 \times 10^4$ A/cm², 77 K, 0 T) is reported. The experimental results show that powder packing densities and annealing temperature have important influence on J_c . The character of J_c under applied magnetic field is analyzed.

1. Introduction

Since the discovery of high- T_c superconducting oxides much effort has been made on the fabrication technique of HTSC composite wires to make them available to applications. As an example, Bi(2223)/Ag tape with J_c ($= 6.6 \times 10^4$ A/cm², 77 K, 0 T; 1.45×10^4 A/cm², 77 K, 1 T) has been obtained by Yamada et al. [1]. As far as the Tl-Ba-Ca-Cu-O superconductor is concerned, though its T_{c0} (125 K) is the highest attained so far, because of the toxicity of the easily vaporizing thallium, the research of the fabrication process of the Tl-system composite tape is not as extensive as that of the Bi system. Lee et al. [2] have reported that the Tl-system superconductor has pinning as strong as the Bi-system superconductor at low temperatures. For this reason, we have investigated the fabrication and properties of Tl-system Ag-sheathed tape.

2. Experimental Technique

The preparation of Tl-Ba-Ca-Cu-O 2223 single-phase bulk samples with $T_{c0} = 120$ K is described in [3]. The 2223 single-phase pellets were pulverized and packed into three pieces of silver tube (6 mm in diameter, 1.2 mm thick, 100 mm long). Three composite bars were fabricated by swaging with the powder packing densities of 3.8, 4.8, and 6.0 g/cm³. They were drawn to wires with 0.85 mm diameter and pressed into tapes with thickness from 0.12 to 0.16 mm. The tapes were sintered from 630 to 870 °C for periods of 5 min to 1 h in air.

The measurement of critical transport current was carried out by the standard four-probe method. The criterion for J_c determination was defined as 1 μV/cm. J_c was also measured in magnetic fields parallel to the surface of the tape up to 0.25 T. The X-ray diffraction

Hefei 230031, People's Republic of China.
 Fayetteville Ark-72701, USA.
 Hefei 230026, People's Republic of China.



ELSEVIER

Physica C 225 (1994) 397-403

PHYSICA C

Low-temperature elastic constants of $Y_1Ba_2Cu_3O_7$

Hassel Ledbetter *

National Institute of Standards and Technology, Boulder, CO 80303, USA

Ming Lei

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Allen Hermann

Department of Physics, University of Colorado, Boulder, CO 80309, USA

Zhengzhi Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 8 December 1993; revised manuscript received 11 March 1994

Abstract

Using ultrasonic methods, we studied the 4–295 K elastic constants of a “good” $Y_1Ba_2Cu_3O_7$ polycrystal. We report the bulk, shear, Young moduli and the Poisson ratio. Except for the Poisson ratio, all elastic constants show smooth temperature behavior. Near T_c , during cooling, the Poisson ratio decreases irregularly. Focusing on the bulk modulus B , we use simple thermodynamics to show that the harmonic-observed decrement at $T=0$ corresponds to expectation, but the temperature effect dB/dT is too large by about a factor of two. We attribute the irregular slope to oxygen-atom reordering. Against many reports, our bulk-modulus value is approximately that found in monocystals or that predicted by an ionic-crystal model calculation.

1. Introduction

Elastic constants provide valuable information about material behavior. On one side, elastic constants relate directly to the interatomic potential [1]. On another, they relate to practical problems such as stress-strain, residual stress, and fracture [2]. All processes that couple with strain affect the elastic constants.

Elastic constants provide a sensitive probe of phase transitions: electronic, magnetic, crystal structure [3].

They are key parameters in Landau's theory of second-order phase transitions [4]. In the theory of cooperative Jahn-Teller transitions, they occupy a central place [5].

For superconductors, elastic constants play additional key roles. Consider the now-classic BCS expression for the normal-superconductive transition temperature:

$$T_c = 0.86\theta_D \exp(-\lambda^{-1}). \quad (1)$$

Here, θ_D denotes the Debye temperature, which comes directly from the shear modulus G , atomic volume V_a , and mass density ρ [6]:

* Corresponding author.



Pergamon

Materials Research Bulletin, Vol. 29, No. 10, pp. 1057-1064, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in the USA. All rights reserved
0025-5408/94 \$6.00 + .00

0025-5408(94)00059-X

LIQUID-PHASE-ASSISTED SYNTHESIS OF SINGLE-THALLIUM-LAYER SUPERCONDUCTORS

Y. F. Li, Z. Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701

Nan Chen

Illinois Superconductor Corporation, Evanston, IL 60201

S. E. Dorris, M. T. Lanagan and K. C. Goretta
Argonne National Laboratory, Argonne, IL 60439

(Received July 1, 1994; Refereed)

ABSTRACT

TlBa₂Ca₂Cu₃O_x (Tl-1223) powder was synthesized in O₂ from a mixture of Tl₂O₃ and Ba₂Ca₂Cu₃O_x. The peritectic melting point of Tl-1223 in O₂ is 905°C. It was found that the maximum phase conversion to the Tl-1223 phase occurred at 895-900°C. A small concentration of liquid was present at that temperature. Because of the rapid kinetics of Tl-1223 formation, CaO and BaCuO₂ phases became isolated from the Tl₂O₃ and thus remained in the final microstructure. In samples heated at 895°C, the CaO and BaCuO₂ proved to be sufficiently small to act as flux-pinning sites.

MATERIALS INDEX: oxide, thallium, cuprate, superconductor

Introduction

Tl-based superconductors are highly promising for many high-current superconducting applications. The combination of their high superconducting transition temperature (T_c) [1-3], inherently good properties in a magnetic field [4,5], and possibility for good transport currents in true polycrystalline conductors [6-11] has no equal among high- T_c superconductors. TlBa₂Ca₂Cu₃O_x (Tl-1223) and its alloys have been emphasized because they exhibit the best critical current density (J_c) in applied magnetic fields [4-11].

The Tl-1223 phase can be formed directly [9-13], or by loss of Tl from Tl₂Ba₂Ca₂Cu₃O_x or Tl₂Ba₂CaCu₂O_x [14], possibly in < 1 h. The rapid kinetics are associated with presence of either Tl₂O vapor or Tl-rich liquid [8,12-17]. In contrast, Bi-based superconductors do not generally form such vapors or liquids,

A new 1223-type high T_c cuprate (Tl, V) $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$

Z.Y. Chen*, Z.Z. Sheng, Y.Q. Tang**, Y.F. Li, D.O. Pederson

Department of Physics, University of Arkansas, 105 Physics Building, Fayetteville, AR 72701, USA

Received: 24 March 1993

Abstract. A new 1223-type (Tl, V)-based superconducting layered cuprate $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ with $x = 0.25$ and 0.50 has been successfully synthesized in the nearly-pure form and identified by powder X-ray diffraction analyses. An excessive quantity of Tl is necessary for the preparation of the (Tl, V)-based 1223-type compound. Resistance and ac susceptibility measurements showed that the new (Tl, V)-based 1223 cuprate exhibits T_c above 110 K.

PACS: 74.70. - b; 74.70.Vy; 74.60.Mj

Introduction

It is very interesting that Cr has the capability to form Tl-based superconducting compounds by partially substitution for Tl. We synthesized 1201 phase (Tl, Cr) Sr_2CuO_5 with T_c of 40–50 K [1] and 1212 phase (Tl, Cr) $\text{Sr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ with T_c up to about 110 K [2]. Recently, we successfully synthesized 1223 phase (Tl, Cr) $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ with T_c above 100 K [3]. On the other hand, V also has the capability to promote the formation of superconducting cuprates. For example, we observed that V-doping can significantly increase T_c of the TlSrCuO system [4] and can promote the formation of (Bi, Pb, V)-2223 phase [5]. In addition, 1212 phase (Tl, V) $\text{Sr}_2\text{CaCu}_2\text{O}_7$ was reported by Liu et al. [3]. In view of the synthesis of (Tl, Cr)-1223 cuprate and the similarity in chemical properties of Cr and V, we surmise (Tl, V)-1223 cuprate could also be synthesized. We carried out a series of experiments and successfully synthesized a new 1223-type cuprate (Tl, V) $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ in the nearly-pure form with T_c up to 110 K. In this paper, we report the preparation of this new (Tl, V)-1223 cuprate, and we present the results from powder X-ray diffraction

analyses and from resistance and ac susceptibility measurements.

Experimental

Samples with nominal composition of $(\text{Tl}_2\text{V}_x)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ($x = 0.00, 0.10, 0.25$ and 0.50) were prepared using high-purity Tl_2O_3 , V_2O_5 , SrO, CaO and CuO powders by a two-step solid state reaction method. A $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ precursor was prepared first, and Tl_2O_3 and V_2O_5 were then added. Excess Tl was used to compensate Tl loss during heating by vaporization. In a typical procedure, appropriate amounts of SrO, CaO, CuO were mixed and ground well in an agate mortar. The mixture powder was preheated at 840 °C for 24 h in air atmosphere and then cooled to room temperature. The product was again ground, and subjected to another heating cycle. This procedure was repeated 2–3 times to obtain a uniform powder. Then, the resultant precursor powder was mixed with appropriate amounts of Tl_2O_3 and V_2O_5 , and pressed into pellets of about 12 mm in diameter and about 2 mm in thickness with a hydraulic press. The pellets were placed in a covered alumina crucible, introduced into a preheated tube furnace, and heated at 980 °C in flowing oxygen atmosphere for 5 h. Finally, the temperature of the furnace was decreased naturally to room temperature.

Powder X-ray diffraction measurements were performed with Cu-K α radiation using a DIANO DTM 1057 diffractometer. Resistance was measured by the typical four-probe technique with an AC frequency of 27 Hz. The sample was connected to the leads using silver paste. AC susceptibility was measured by the standard mutual inductance method with an ac frequency of 500 Hz. All measurements were carried out in a commercial APD refrigerator with computer control and processing.

Results and discussion

(Tl, V)-based 1223 phase does not form easily. After extensive experiments, we found that an excess quantity of

* Permanent address: Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

** Permanent address: Analysis and Research Center, East China Institute of Chemical Technology, Shanghai, 200237, People's Republic of China

Research on Tl-based Superconductors at the University of Arkansas

Z. Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

ABSTRACT

We discovered the Tl-Ba-Cu-O system in October 1987 and the Tl-Ba-Ca-Cu-O system in February 1988. The latter still holds the record of the highest reproducible T_c of 125 K. Thereafter, we discovered a number of new Tl-based superconductors, and developed several new processes for the Tl-based superconductors. A number of related patents have been granted.

INTRODUCTION

The discovery of 35 K superconductivity in the La-Ba-Cu-O system by Bednorz and Muller in 1986¹⁾ led to a sudden burst of research activity on oxide superconductivity. Soon 90 K superconductivity in the Y-Ba-Cu-O system was discovered in January 1987²⁾. The latter discovery brought T_c , for the first time, to above liquid nitrogen temperature and allowed most laboratories in the world to carry out the research on superconductivity. Our research on high T_c superconductors was started at this time and formally started in May 1987. We had had an exciting time for nine months. In October 1987, we discovered the 90 K Tl-Ba-Cu-O system, the first superconductor without a rare earth with T_c above 77 K^{3,4)}. In the beginning of February 1988, we discovered the 125 K Tl-Ba-Ca-Cu-O system, the highest T_c superconducting system to date^{5,6)}. After the details of the Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O superconductors were presented at the World Congress on Superconductivity held at Houston, Texas, on February 20-24, 1988⁷⁾, the study on Tl-based superconductors was carried out by many groups all over the world. In this paper, we briefly describe the research on Tl-based superconductors thereafter at the University of Arkansas, including the discovery of new Tl-based superconductors and the development of new processes for Tl-based superconductors. We also give current status of the patents of the University of Arkansas on the Tl-based superconductors

NEW TL-BASED SUPERCONDUCTORS

The Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O systems were discovered, somewhat, based on the idea of substitutions with metals of same valence and similar ionic radius³⁻⁷⁾. The discovery of the Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O systems provided many substitutions which may lead to new Tl-based superconductors.

New high- T_c cuprate $(\text{Tl}_{1-x}\text{Cr}_x)(\text{Sr}_{2-y}\text{Ba}_y)\text{Ca}_2\text{Cu}_3\text{O}_9$

Z. Y. Chen,^{a)} Z. Z. Sheng, Y. Q. Tang, Y. F. Li, L. M. Wang,^{b)} and D. O. Pederson
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 22 December 1992; accepted for publication 19 March 1993)

A new series of 1223-type (Tl,Cr)-based cuprates, $(\text{Tl,Cr})(\text{Sr,Ba})_2\text{Ca}_2\text{Cu}_3\text{O}_x$, have been successfully synthesized and identified by powder x-ray diffraction and electron diffraction analyses. Ba partial substitution for Sr promotes the formation of (Tl,Cr)-based 1223-type compounds. Nominal samples, $(\text{Tl}_{1-x}\text{Cr}_x)(\text{Sr}_{2-y}\text{Ba}_y)\text{Ca}_2\text{Cu}_3\text{O}_x$, with $0.15 < x < 0.50$ and $0.50 < y < 1.50$ are pure or nearly pure 1223 phase and exhibit $T_c(\rho=0)$ in the range of 104–114 K. This new (Tl,Cr)-based high- T_c material may be of importance in practical applications.

After the TlBaCaCuO superconducting system was discovered,^{1,2} and $(\text{TlO})_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ with $m=2$ and 1 was identified,^{3,4} the TlSrCaCuO system was found to be also superconducting at 20 and 70 K.⁵ In fact, there is a series of superconducting compounds in the TlSrCaCuO system: $(\text{TlO})_m\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ with $m=1$ and $n=1-3$.⁶ The Sr series compounds are not easy to form. But, by partially substituting Pb for Tl, the 1223 phase $(\text{Tl,Pb})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ forms easily and T_c is as high as 122 K.⁷ Multi-phase nominal samples $(\text{Tl,Bi})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ were reported with T_c (onset) of 119 K and $T_c(\rho=0)$ of 106 K,⁸ which may originate from a (Tl,Bi)-1223 phase. After that, 1223-type compounds, for example, 120 K $(\text{Tl,Pb,Bi})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$,⁹ 115 K $(\text{Tl}_{1-x}\text{Bi}_x)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$,¹⁰ 114 K $(\text{Tl}_{0.45}\text{Pb}_{0.5})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{8.2}$,¹¹ and 120 K $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ (Ref. 12) were reported. Recently, the Tl-based 1223 compounds received special attention because they were found to have a very high critical current density at 77 K compared with Tl-2223 or Bi-2223 superconductors according to the magnetic hysteresis measurements.¹³ Tl-1223 superconductors actually have less anisotropy compared with other cuprate superconductors due to stronger interlayer coupling between CuO_2 planes because of the presence of only a single insulating (TlO) layer in the compound, leading to an enhanced coupling along the c -axis and hence to a three-dimensional charge transfer character, rather than the two-dimensional character of the Tl-2223 compound.¹³⁻¹⁵ Therefore, Tl-1223 is an excellent compound of choice for fabricating Ag- or (Au,Pd)-sheathed superconducting wires and tapes by the powder-in-tube process.¹⁶⁻¹⁸

Because Cr has the capability to promote the formation of superconducting phases and to increase T_c in Cr-substituted 1201-phase $\text{TlSr}_2\text{CuO}_5$ (Ref. 19) and Cr-substituted 1212-phase $\text{TlSr}_2\text{CaCu}_2\text{O}_7$,^{20,21} we carried out a series of experiments to synthesize Cr-substituted 1223-phase $\text{TlSr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$. The results showed that the (Tl,Cr)-1223 phase $(\text{Tl,Cr})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ is rather difficult

to synthesize, but when Sr is partially substituted by Ba, the 1223 phase forms easily. In this letter we report the preparation of the new 1223-type cuprate $(\text{Tl,Cr})(\text{Sr,Ba})_2\text{Ca}_2\text{Cu}_3\text{O}_9$ in the pure or nearly pure form and the characterization by x-ray diffraction and electron diffraction. Their $T_c(\rho=0)$ are in the range of 104–114 K. This new (Tl,Cr)-based 1223-type high- T_c material may be of importance in practical applications.

Samples with nominal compositions $(\text{Tl}_{1-x}\text{Cr}_x)(\text{Sr}_{2-y}\text{Ba}_y)\text{Ca}_2\text{Cu}_3\text{O}_x$ ($x=0.00, 0.25, 0.50$; $y=0.1, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00$) were prepared using high-purity Tl_2O_3 , Cr_2O_3 , SrO, BaO_2 , CaO, and CuO powders by a two-step solid-state reaction method. Tl_2O_3 was excessive by 20% to compensate Tl loss by vaporization. In the typical procedure, precursors $(\text{Sr}_{2-y}\text{Ba}_y)\text{Ca}_2\text{Cu}_3\text{O}_x$ were prepared first. Appropriate amounts of SrO, BaO_2 , CaO, and CuO were mixed and ground well in an agate mortar. The mixture powders were preheated at 840 °C for 24 h in an air atmosphere and then cooled to room temperature. The products were again ground, and were subjected to another heating cycle. This procedure was repeated two to three times to obtain a uniform powder. Then, the resultant precursor powders were mixed with appropriate amounts of Tl_2O_3 and Cr_2O_3 , ground, and pressed into pellets of about 12 mm in diameter and about 2 mm in thickness with a hydraulic press. The pellets were placed in a covered alumina crucible, introduced into a preheated tube furnace and heated at 900–1000 °C in flowing oxygen atmosphere for about 5 h. Finally, the temperature of the furnace was decreased naturally to room temperature.

Powder x-ray diffraction measurements were performed with $\text{CuK}\alpha$ radiation using a DIANO DTM 1057 diffractometer. The samples were also examined in detail using a JEM 2000FX analytical electron microscopy with a TN-5500 energy-dispersive x-ray spectroscopy (EDXS) analyzer. Resistance was measured by the typical four-probe technique with an ac frequency of 27 Hz. The sample was connected to the leads using silver paste. All measurements were carried out in a commercial APD refrigerator with computer control and processing.

We first tried to prepare samples with a 1223 starting composition $(\text{Tl}_{1-x}\text{Cr}_x)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$. But the samples prepared by the typical procedure do not easily form the 1223 phase. Rather, when $x=0.1-0.5$, the samples mainly form the 1212 phase and exhibit T_c around 100 K, which

^{a)}Permanent address: Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China.

^{b)}Present address: Department of Geology, University of New Mexico, Albuquerque, NM 87131.

Superconducting $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ thin films with critical current density up to 10^6 A/cm^2

Y. Q. Tang, K. Y. Chen, I. N. Chan, Z. Y. Chen, Y. J. Shi, G. J. Salamo, F. T. Chan, and Z. Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 8 March 1993; accepted for publication 13 June 1993)

Superconducting $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ thin films with zero resistance temperature T_c up to 102 K and critical current density J_c as high as 10^6 A/cm^2 at 77.7 K have been successfully prepared via laser ablation and thallium diffusion. Prolonged low temperature annealing in air was used for film processing. X-ray diffraction patterns indicated that the films were highly oriented 1212 phase with c axes normal to the $\text{LaAlO}_3(100)$ or $\text{MgO}(100)$ substrates.

Among the Tl-based high T_c superconductors,¹⁻⁴ the single Tl-O layered Tl-1212 and Tl-1223 compounds have drawn more and more attention in applied superconductivity.⁵⁻⁷ Since the distance between Cu-O conducting planes in these compounds is shorter than in the compounds with two Tl-O layers (2212 and 2223), leading to stronger interlayer coupling, it is suggested that the thermally activated flux motion in Tl-1212 and Tl-1223 phases may not be as severe as that in double Tl-O layered compounds.⁸ It is also believed that the single Tl-O layered compounds have higher critical current density J_c and their superconducting performances are less influenced by magnetic field.^{5,8,9} These advantages make Tl-1223 and Tl-1212 phases good candidates for the fabrication of superconducting wires and thin films.

Based on the work of the 105 K $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ bulk material in which Cr primarily takes the position of Ca,¹⁰ we have recently prepared this kind of 1212 phase film by chemical deposition¹¹ and by laser ablation.¹² It was found that the new 1212 films were easy to prepare and could sustain a wide range of processing conditions. However, the superconducting properties of the films should be further improved in order to meet the requirements of practical application.

In this communication, we report the preparation of highly oriented Cr-substituted 1212 phase $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ films of good quality. The films were produced by a two-step process via laser ablation and post-annealing in Tl vapor. By carefully controlling annealing conditions, we have successfully obtained superconducting $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ films with T_c of 98–102 K and J_c of $1 \times 10^6 \text{ A/cm}^2$ at 77.7 K. To our knowledge, the J_c value is among the highest values achieved in 1212 phase Tl-based thin films.

The precursor films with a fixed starting composition of $\text{Sr}_2\text{CaCr}_{0.2}\text{Cu}_2\text{O}_z$ were first deposited onto $\text{MgO}(100)$ or $\text{LaAlO}_3(100)$ substrates using an Ar-F excimer laser. This starting composition was chosen according to the optimum range of Cr amount in the nominal compositions $\text{TlSr}_2\text{CaCr}_y\text{Cu}_2\text{O}_z$ ($y=0.15-0.25$) of bulk material.¹⁰ The laser operated with a wavelength of 193 nm at 10 Hz. The pulse energy was 125 mJ. The oxygen pressure in the deposition chamber was 200 mTorr and the deposition time was 20–30 min. The substrate temperature was controlled

in the range of 250–350 °C during ablation. It was found that the substrate temperature was not critical during deposition as long as it was lower than 600 °C. With a thickness of 0.3–0.8 μm , the precursor films had a dark brown color and looked mirror-like.

The as-deposited precursor films were then annealed in Tl vapor. One unfired pellet with the nominal composition $\text{Tl}_x\text{Sr}_2\text{CaCr}_{0.2}\text{Cu}_2\text{O}_z$ ($x=1$ or 1.3) was used as the main Tl vapor source, and some fired pellets were used as supports and as an auxiliary Tl source. We determined that $x=1$ in the nominal composition corresponded to the ideal Tl amount for synthesizing the 105 K 1212-phase bulk material. This ratio did not seem adequate for prolonged film annealing. Therefore, $x=1.3$ was chosen to enhance the concentration of Tl vapor during the annealing process. Two kinds of slightly different configurations were used in the film annealing. One was the so-called “untouched method,” in which the unfired pellet was placed about 1 mm above the precursor film in a covered alumina boat. The other was called the “touched method,” where the film was sandwiched between two pellets vertically placed in a closed alumina cylinder with the film surface confined to the unfired pellet. Annealing was carried out in a programmable tube furnace at 860–870 °C, about 50 °C lower than the calcining temperature for bulk material.¹⁰ A lower annealing temperature proved to be helpful in improving the properties of superconducting films.^{13,14} A cooling rate as low as 2 °C/min was used to ensure the final film quality.¹² The T_c and J_c of the fabricated superconducting films were then measured either by the four-probe or by the self-inductance¹⁵ method.

In previous work, annealing was carried out in a flowing oxygen atmosphere for less than 3 h and the nominal $\text{TlSr}_2\text{CaCr}_{0.2}\text{Cu}_2\text{O}_z$ pellets were used as a Tl vapor source.^{11,12} In the present work, however, we annealed the films in air and prolonged the annealing time to 5–20 h. These modifications played an important role in improving the quality of the resulting films. Studies on the effect of oxygen pressure on the formation of Tl-based superconductors show that the decrease of oxygen pressure can reduce the temperature of phase formation and enable the reaction at lower temperature.^{14,16} The oxygen pressure in air (0.2 atm) is much lower than the 1 atm flowing oxygen; thus, the formation of superconducting film at low anneal-

Thermoelectric power of the thallium-based superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$

Y. Xin, K. W. Wong, and C. X. Fan

Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66045

Z. Z. Sheng and F. T. Chan

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 9 November 1992; revised manuscript received 3 March 1993)

The temperature dependence of the thermoelectric power of the high-temperature superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$ is reported. The contribution of holes from the valence band satisfying a Fermi-liquid model gives the major part of the measured thermoelectric power. The results show that the conduction-band electrons also contribute to the total output of the thermoelectric power and the portion of the electron's contribution increases with temperature. An explicit expression for the thermoelectric power of the 2:2:2:3 phase was derived based on a two-band model and the experimental data, which is given as $S(\mu\text{V}) = 0.121T - (280 - 0.2T)e^{-550/T}$. A general formula, $S = AT + (B\lambda + CT)\exp(-\lambda/T)$, is found to give a close description of the thermoelectric power of various cuprate high- T_c superconductors.

The absolute thermoelectric power S is an excellent indicator of many fundamental aspects of charge transport in a conducting material. We can extract useful information from the characteristics of S -temperature dependency to reveal the normal-phase transport mechanism of a material. Furthermore, the sign of S can be used to distinguish the major charge carrier in the transport process. In certain regimes, S can also provide knowledge for the bandwidths and band gaps which govern the transport properties of the material.

Since the discovery of high- T_c superconductors, there have been a large number of experimental and theoretical efforts to understand the thermoelectric power of such a material. However, a satisfactory interpretation of experimental results are still lacking. $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$ is a very stable superconductor with a transition temperature above 120 K, which is the highest to date. Several groups¹⁻³ have studied the thermoelectric power of Tl-based compounds, including the 2:2:2:3 phase; but, unfortunately, a quantitative study is far from complete due to a lack of single phase samples. We carried out thermoelectric power study on a very pure 2:2:2:3 phase sample in a quantitative manner. Based on the experimental result, we propose a two-band (conduction CB, valence VB) conduction mechanism and give an explicit expression of the thermoelectric power of the Tl-based superconductor. This theoretical expression may also be applied to other high- T_c superconductors.

Samples used in this study were prepared by our recently developed method.⁴ The sample $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$ is a pure 2:2:2:3 phase sample (no impurity being detected by powder x-ray diffraction). The thermoelectric power was measured with a modified differential method⁵ in the temperature range from 300 to 100 K.

Figure 1 shows the S plot against temperature of the sample $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$. At room temperature, the value of S for this sample is $1.8 \mu\text{V}/\text{K}$ and S increases al-

most linearly with decreasing temperature. It has a maximum value of $12.3 \mu\text{V}/\text{K}$ at about 135 K and drops abruptly as T approaches T_c . These values are to be compared to those in Ref. 5 and will be discussed later.

The thermoelectric power-temperature dependency of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$, as viewed from the overall behavior, is similar to those reported for $(\text{La,Sr})_2\text{CuO}_{4-\delta}$, $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = rare earth), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$, and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-\delta}$.⁶⁻¹⁵ To explain the temperature dependence of S and the exhibition of a broad maximum above T_c for these high- T_c materials, some groups suggested a model of a strong phonon-drag effect,¹⁶⁻¹⁸ while others expressed a strong doubt on this suggestion.^{19,20} Based on our experimental data, there appears to be no evidence in support of phonon-drag contribution to the thermoelectric power. We found that the thermoelectric power can be simply explained from the diffusion of the charge carriers.

A specific formula for the thermoelectric power of a metal satisfying the Fermi liquid model, due to electron

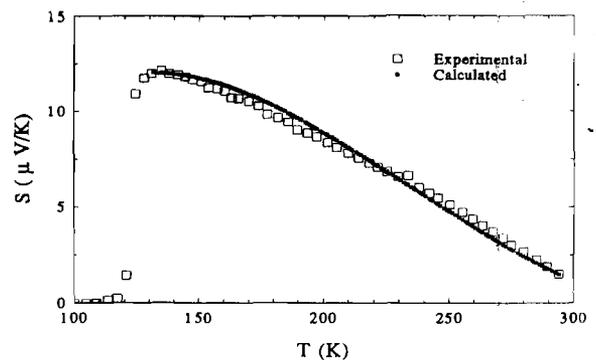


FIG. 1. Thermoelectric power vs temperature of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$.

Synthesis and superconductivity of a new 1222-type Tl-based layered cuprate (Tl, Nb) Sr₂(Nd, Ce)₂Cu₂O_z

Z.Y. Chen*, Y.Q. Tang**, Y.F. Li, D.O. Pederson, Z.Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received: 15 May 1992/Revised version: 18 August 1992

Abstract. Synthesis and superconductivity of a new 1222-type layered cuprate (Tl_{1-x}Nb_x) Sr₂(Nd_{1-y}Ce_y)₂Cu₂O_z have been studied. The structure of this cuprate is directly related to that of Nb-1222 NbSr₂(Nd, Ce)₂Cu₂O_z with tetragonal body-center lattice. Partial substitution of Tl for Nb in Nb-1222 phase improves its superconductivity. (Tl_{1-x}Nb_x) Sr₂(Nd_{0.75}Ce_{0.25})₂Cu₂O_z samples prepared by the typical procedure exhibit superconductivity with T_c of 30–40 K. Effects of Tl and Nb on superconductivity of this cuprate are briefly discussed.

1. Introduction

Li et al. [1, 2] reported the synthesis and possible superconductivity of a new 1222 type layered cuprate MSr₂(Ln, R)₂Cu₂O_z (M = Ta, Nb, and Ti; Ln = Nd and Pr; R = Ce and Th) by La₂O₂ double layers replacing single LaO layer in LaBa₂Cu₂TaO_y, which was first prepared by Murayama et al. [3]. The structure of the new cuprate (Nb-1222) is directly related to that of (Pb, Cu)-Sr₂(Ln, Ce)₂Cu₂O_z, (Pb-1222) [4], TlBa₂Ln₂Cu₂O_z, (Tl-1222) [5] and (Ln, Ce)₂(Ln, Ba)₂Cu₃O_y, (Cu-1222) [6] with M occupying the Pb, Tl or Cu site. Soon after the discovery of the Nb-1222 compound, Cava et al. reported superconductivity with T_c of 28 K for NbSr₂(Nd_{0.75}Ce_{0.25})₂Cu₂O₁₀ [7]. However, superconductivity is observed only for a narrow range of oxygen pressures, temperatures, annealing times, and cooling rates, including the need for striking a delicate balance among solid solubility, cation ordering, and oxygen content. Recently we successfully synthesized a new Tl-based 1222-type layered cuprate (Tl_{0.8}M_{0.2})Sr₂(Nd_{0.75}Ce_{0.25})₂Cu₂O_z (M = Nb or Ti) with T_c of about 40 K [8]. Further

experiments showed that a whole series of compounds (Tl_{1-x}Nb_x)Sr₂(Nd_{1-y}Ce_y)₂Cu₂O_z can be synthesized in the nearly pure form. In this paper, we report in detail the synthesis and superconductivity of the serial compounds (Tl_{1-x}Nb_x)Sr₂(Nd_{1-y}Ce_y)₂Cu₂O_z. We will also briefly discuss the effect of Tl/Nb ratio and Nd/Ce ratio in this series of compounds on superconductivity.

2. Experimental

Samples were prepared by a two-step solid state reaction method. High purity Tl₂O₃ (or Tl₂CO₃), NbO (or Nb₂O₅), SrO, Nd₂O₃, CeO₂ and CuO were mixed according to the stoichiometric formula (Tl_{1-x}Nb_x)Sr₂(Nd_{1-y}Ce_y)₂Cu₂O_z with x = 0.0, 0.2, 0.4, 0.6, and 0.8; y = 0.0, 0.25, 0.5, 0.75, and 1.0. First, appropriate amounts of the component oxides except Tl₂O₃ (or Tl₂CO₃) were mixed and ground in an agate mortar. The resulting powder was then pressed into pellets of about 12 mm in diameter and about 2 mm in thickness with a hydraulic press. The pellets were sintered at 1000 °C for 24 h in air followed by very fast cooling to room temperature. This procedure was repeated several times to obtain a uniform powder. After thoroughly grinding, the powder was mixed with an appropriate amount of Tl₂O₃ (Tl₂CO₃) and was again pressed into new pellets. The new pellets were placed in a covered alumina crucible, introduced into a preheated tube furnace and heated at 1000–1100 °C in flowing oxygen atmosphere for 10–30 min. The temperature of the furnace was then decreased gradually to 800–850 °C, held at that temperature for about 1–5 h, and finally decreased to room temperature. (Tl, Nb)Sr₂(Nd, Ce)₂Cu₂O_z samples were also prepared directly from mixing component oxides or carbonates according to the stoichiometric composition (one-step solid state reaction method.) The Tl-free sample NbSr₂(Nd, Ce)₂Cu₂O_z was prepared using the procedure recommended by [1].

The resulting samples were subjected to powder X-ray diffraction analyses and resistance measurements.

* Permanent address: Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

** Permanent address: Analysis and Research Center, East China Institute of Chemical Technology, Shanghai 200237, People's Republic of China

Effects of Bi-substitution for Tl in 1222-type cuprate $\text{TlSr}_2(\text{Nd}, \text{Ce})_2\text{Cu}_2\text{O}_z$

Z.Y. Chen, Z.Z. Sheng, Y.Q. Tang, Y.F. Li and D.O. Pederson
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

K. Goretta ^a, P. Kostic ^b and D.L. Shi ^b

^a *Materials and Components Technology Division*

^b *Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*

Received 23 November 1992

Revised manuscript received 6 April 1993

Bi may substitute Tl in the 1222-type cuprate $\text{TlSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ up to 80%. The Tl-free Bi-1222 cuprate does not form even from a Bi-1222 starting composition. The *c*-axis and cell volume of the (Tl, Bi)-1222 cuprate decrease with the increase of the amount of Bi. Resistance measurements showed that Bi substitution for Tl converts superconducting $\text{TlSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ to semiconducting $(\text{Tl}_{1-x}\text{Bi}_x)\text{Sr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ ($x \geq 0.2$). These results are discussed according to the concept of mixed Cu valence.

1. Introduction

Soon after Li et al. [1,2] discovered the 1222-type cuprate $\text{NbSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$, Cava et al. [3] made it superconducting at about 28 K by annealing under high O_2 pressure. Meanwhile, we were able to synthesize a Tl-based 1222-type cuprate $\text{TlSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ through Tl replacing Nb, which is superconducting at about 40 K [4,5]. The Tl-based 1222 cuprate can be subjected to extensive elemental substitutions, forming a series of (Tl, M)-based 1222 cuprates $(\text{Tl}_{1-x}\text{M}_x)\text{Sr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$, where M is a metallic element, for example Pb [6] or In [7]. In this paper, we report effects of Bi substitution for Tl in the 1222-type cuprate $\text{TlSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ on the phase formation and superconductivity. The results from X-ray diffraction analyses and resistance measurements are presented and are discussed according to the concept of mixed Cu valence.

2. Experimental

Samples were prepared by the solid-state reaction method. High purity Tl_2CO_3 (or Tl_2O_3), Bi_2O_3 , SrO , Nd_2O_3 , CeO_2 and CuO were used according to the stoichiometric formula $(\text{Tl}_{1-x}\text{Bi}_x)\text{Sr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ with $x=0.0, 0.2, 0.4, 0.6$ and 0.8 . Tl_2CO_3 or Tl_2O_3 is in excess by about 10–15%, because of the volatility of Tl compounds. Appropriate amounts of the component oxides (or carbonate) were mixed and ground well in an agate mortar. The resulting powder was pressed into pellets about 12 mm in diameter and about 2mm in thickness with a hydraulic press. The pellets were placed in a covered alumina crucible, introduced into a preheated tube furnace and heated at 900–1050°C in flowing oxygen atmosphere for 30–60 min. The temperature of the furnace was then decreased gradually to 850°C and held for about 5 h. Finally, the temperature of the furnace was decreased to room temperature. The Tl-free sample was prepared using the procedure recommended in ref. [1].

The powder X-ray diffraction measurements were performed with Cu $K\alpha$ radiation using a DIANO

Phase transformation during low temperature Tl-diffusion in the fabrication of Tl-Ba-Ca-Cu-O thin films

Y.Q. Tang, Z.Z. Sheng, W.A. Luo, I.N. Chan, Z.Y. Chen, Y.F. Li and D.O. Pederson

Physics Department, University of Arkansas, Fayetteville, AR 72701, USA

Received 1 April 1993

Revised manuscript received 10 June 1993

In the two-step fabrication of Tl-Ba-Ca-Cu-O thin films, $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) and $Tl_1Ba_2Ca_2Cu_3O_9$ (Tl-1223) films with good superconducting properties can be produced at a relatively low Tl-diffusion temperature. Our study shows that although a low annealing temperature generally favors the formation of $Tl_2Ba_2Ca_1Cu_2O_7$ (Tl-2212) superconducting film, Tl-2223 and Tl-1223 phases can still form by prolonging the annealing time. In fact, a prolonged annealing time leads to the transformation from Tl-2212 phase to Tl-2223 phase, and then to Tl-1223 phase. Therefore, the annealing time must be carefully controlled to get the needed superconducting phase.

1. Introduction

Since the discovery of Tl-based superconductors [1,2] more and more attention has been paid to this system. Among various Tl-based compounds, two of them are of particular interest. One is a double Tl layer $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) having a T_c as high as 127 K and another is a single Tl layer $Tl_1Ba_2Ca_2Cu_3O_9$ (Tl-1223) oxide which, due to stronger interlayer coupling between the Cu-O planes and relatively high T_c (above 110 K), is believed to have better superconducting properties in a magnetic field than other Tl-compounds [3].

In the direct synthesis of bulk material, the reaction temperature for forming different phases is generally in the order Tl-1223 > Tl-2223 > Tl-2212. Tl-1223 oxide needs a reaction temperature as high as 925°C while Tl-2212 can form at a temperature around 830°C. Some authors have suggested the sequential transformations Tl-2212 → Tl-2223 → Tl-1223 → Tl-1234 as a reaction pathway for bulk samples [4-6]. These transformations can be realized either by increasing the reaction temperature by stages [7] or by reducing the Tl content in the starting composition [4,5]. An increasing reaction time was also found to be useful in converting double Tl layer compounds into single Tl layer compounds [8].

Two transformation mechanisms were proposed [5]. In both explanations, the variation of the Tl content during the reaction plays a crucial role in the phase transformation.

In the fabrication and application research of Tl-based thin films, Tl-2223 and Tl-1223 films also draw intensive study due to the same reasons mentioned above [9-11]. Unlike the Tl-1212 phase thin film which can be successfully obtained via in-situ one step deposition [12], post-deposition annealing in the presence of Tl vapor is still a necessary procedure for the preparation of Tl-2223 and Tl-1223 thin films, and is a crucial step for film quality. The annealing temperature, the Tl vapor concentration and the annealing time are all very important factors controlling the morphology, superconducting phase, T_c and J_c of the thin films. Some recent studies show that prolonged lower temperature annealing can produce a high quality Tl-2223 film [10,13]. In this paper, we investigate and discuss the formation of Tl-2223 and Tl-1223 films via phase transformation at a relatively low annealing temperature. The properties of the corresponding Tl-2223 and Tl-1223 films will also be presented.

Synthesis and characterization of 2234-phase $Tl_2Ba_2Ca_3Cu_4O_{12}$ prepared near and at the melting point

Z Y Chen†, Z Z Sheng, Y Q Tang, Y F Li, L M Wang‡ and D O Pederson

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

Received 17 December 1992

Abstract. Bulk samples of nearly-pure 2234-phase $Tl_2Ba_2Ca_3Cu_4O_{12}$ were synthesized near the melting point from starting compositions of either $Tl_2Ba_2Ca_{3.3}Cu_4O_x$ or $Tl_2Ba_2Ca_4Cu_5O_x$. Well crystallized 'clusters' of 2234-phase $Tl_2Ba_2Ca_3Cu_4O_{12}$ were also prepared by melting the starting material $Tl_2Ba_2Ca_4Cu_5O_x$. The 2234-phase samples prepared in the present experiment exhibit $T_c(\rho = 0)$ up to 119 K.

1. Introduction

After the 120 K superconductivity in the Tl-Ba-Ca-Cu-O system was discovered [1, 2], a series of superconductors with a general formula $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ was identified [3-5]. It was immediately found that their T_c increased with n (the number of CuO_2 layers): 90 K for $Tl_2Ba_2CuO_6$ (2201 phase) with one CuO_2 layer, 110 K for $Tl_2Ba_2CaCu_2O_8$ (2212 phase) with two CuO_2 layers, and 125 K for $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223 phase) with three CuO_2 layers. It was natural to surmise that the members with more CuO_2 layers could reach even higher T_c . An extensive search was carried out and the members with $n > 3$ were synthesized, but they did not exhibit higher T_c [6]. The highest T_c remains 125 K for the member with $n = 3$ (2223 phase $Tl_2Ba_2Ca_2Cu_3O_{10}$) to date. The fact that T_c increases with the number of CuO_2 layers (up to three CuO_2 layers) is still one of the guidelines in searching for higher T_c perovskite-type superconductors. The 2234 phase $Tl_2Ba_2Ca_3Cu_4O_{12}$ with four CuO_2 layers is an immediate candidate. Due to preparation difficulties progress is slow [7-9]. Recently Presland *et al* [10] prepared a single-phase Tl-2234 bulk superconductor, $Tl_{2-x}Ba_2Ca_{3.3}Ca_4O_{12}$, which exhibits a diamagnetic transition up to 116 K by oxygen loading or prolonged vacuum annealing. We have prepared nearly-pure 2234 phase near the melting point from starting compositions $Tl_2Ba_2Ca_{3.3}Cu_4O_x$ or $Tl_2Ba_2Ca_4Cu_5O_x$. We have also prepared 2234-phase 'crystal clusters' by melting the starting material

$Tl_2Ba_2Ca_4Cu_5O_x$. The $T_c(\rho = 0)$ of the 2234 phase prepared in the present experiment is up to 119 K. In this paper, we report the preparation procedures and the results from x-ray diffraction, electron microscopy, and resistance measurements.

2. Experimental details

Samples were prepared using high-purity Tl_2O_3 , BaO_2 , CaO and CuO powders according to starting composition $Tl_2Ba_2Ca_{3.3}Cu_4O_x$ and $Tl_2Ba_2Ca_4Cu_5O_x$. The component oxides were mixed and ground well in an agate mortar. The resulting powder was pressed into pellets of about 12 mm diameter and thickness of about 2 mm with a hydraulic press. For the following experiments, we first measured the melting point of the starting materials by heating a pellet in a preheated tube furnace with flowing oxygen atmosphere. The determined melting points in flowing oxygen atmosphere are about 950 °C for the nominal composition $Tl_2Ba_2Ca_{3.3}Cu_4O_x$, and about 960 °C for the nominal composition $Tl_2Ba_2Ca_4Cu_5O_x$. After the melting point was determined, the sample was placed in a covered alumina crucible, introduced into a preheated tube furnace, and heated near or at its melting point in flowing oxygen atmosphere for between 5 min and 16 h. Note that the word 'near' means that the heating temperature used in the work is about 5-10 °C lower than the melting point. The temperature of the furnace was then decreased gradually to 850 °C and held for 24 h. Finally, the temperature of the furnace was decreased naturally to room temperature by turning off the furnace.

Powder x-ray diffraction measurements were performed with Cu-K α radiation using a DIANO DTM

† Permanent address: Department of Applied Chemistry, University of Science & Technology of China, Hefei, Anhui, 230026, People's Republic of China.

‡ Permanent address: Department of Geology, University of New Mexico, Albuquerque, NM 87131, USA.

Preparation of $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films via low-temperature Tl-diffusion

Y Q Tang†, Z Z Sheng†, W A Lout, Z Y Chent, Y N Chant, Y F Lit, F T Chant, G J Salamo†, D O Pederson†, T H Dhayagude‡, S S Ang† and W D Brown†

† Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701 USA

‡ Department of Electrical Engineering, University of Arkansas, Fayetteville, Arkansas 72701 USA

Received 24 November 1992

Abstract. Superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films with T_c ($\rho = 0$) up to 121 K were successfully prepared via the deposition of a BaCaCuO precursor (by laser ablation or sputtering) and thallium diffusion under 1 atmosphere of air. Instead of a short annealing time at high temperature, we use a prolonged annealing time (up to 60 hours) at lower temperature (800–815°C). The films obtained with this procedure are generally good in morphology, highly oriented and exhibit a critical current density, J_c , of about $1\text{--}2 \times 10^6$ A cm⁻² on MgO(100) and up to 1.5×10^6 A cm⁻² on LaAl₃(100) at 77 K. Both T_c and J_c values reported here are comparable to the best Tl-2223 films prepared by the pseudo-one-step process.

1. Introduction

Since the discovery of Tl-based superconductors [1–2], the compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223 or 2223) has been found to have the highest T_c ($\rho = 0$) up to 127 K [3–4]. With high sintering temperature ($> 850^\circ\text{C}$), it is usually not difficult to prepare and reproduce bulk 2223 materials with T_c about 120 K. However, to further improve the T_c , a sophisticated post-annealing procedure, involving low-temperature treatment and oxygen adjusting, must be introduced. By encapsulating the 2223 samples in evacuated quartz tubes and post annealing at low temperatures (750–760°C) for about 10 days or more, the T_c can be increased to 127 K [3–4]. Moreover, reduced partial oxygen pressure has proved useful in decreasing the synthesis temperature of the 2223 phase [5] and in increasing its T_c [3].

In the fabrication of Tl-2223 thin films, where post annealing is still necessary for both pseudo-one-step or two-step processes [6], reduction of annealing temperature is of particular importance because it not only leads to the formation of high-quality films but is also a necessary step towards a real one-step process such as that for Tl-1212 film [7]. Previous annealing procedures for 2223 films generally use high temperatures ($> 850^\circ\text{C}$) and short times (5–60 min), which usually generate relatively rough film surface and poor J_c . Lee *et al* recently reported the low temperature formation of 2223 films in reduced O_2 pressure [8]. With their pseudo-one-step procedure, the quality of the 2223 film was improved significantly. Their best films were shiny to the eye and showed a T_c as high as 121 K and a J_c of 1.6×10^6 A cm⁻² at 77 K. However, their technique

was somewhat complicated. Our recent work on spray pyrolysis also showed that, even under 1 atmosphere of oxygen, 2223 films with T_c up to 121 K can still form at relatively low annealing temperature if the annealing time is long enough [6].

In this paper, we report the two-step formation of 2223 films at low annealing temperature in 1 atmosphere of air. Under optimum conditions, the T_c ranged from 117 K to 121 K, and J_c is $1\text{--}2 \times 10^6$ A cm⁻² for the films on MgO(100) substrates and up to 1.5×10^6 A cm⁻² on LaAlO₃ at 77 K.

2. Experimental details

The substrates used for film production were MgO(100) and LaAlO₃(100). The BaCaCuO precursor films were deposited by laser ablation or sputtering. The details of the equipment for these methods are described elsewhere [9, 10]. The substrates were heated at 400–500°C for the laser ablation but were kept at room temperature during sputtering. The precursor films deposited by laser were 0.4–0.5 µm thick while those by sputtering were about 0.8 µm. Thallium was then introduced by annealing the as-deposited BaCaCuO films with crude $Tl_{1.7}Ba_2Ca_{2.3}Cu_3O_x$ pellets in a closed alumina boat. The films were placed in a free-surface configuration with the pellet positioned about 1 mm above the film. The pellets were prepared using high purity Tl_2O_3 , BaO_2 , CaO and CuO powder [11]. The annealing temperature was 750–820°C, 80–150°C lower than the conventional temperature for bulk formation and at least 50°C lower than the generally used

Effect of Cr and V substitution on the properties of bulk Tl-based superconductors*

M. Pont, T. Puig, J.S. Muñoz, Z.Z. Sheng[†], Y. Xin[†], D.X. Gun[†] and D.O. Pederson[†]

Electromagnetism Group, Department of Physics, Autònoma University of Barcelona, 08193 Bellaterra, Spain

[†]Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Bulk Tl-Ba-Ca-Cu-O superconducting samples have been used to analyse the effect of Cr and V doping on the intergranular properties. The a.c. magnetic susceptibility has been measured as a function of temperature and a.c. magnetic field amplitude up to 14 000 A m⁻¹ as well as the resistivity as a function of temperature and d.c. applied magnetic field up to 795 kA m⁻¹. For the samples doped with Cr an enhancement in the intergranular critical current density was observed; the sample doped with V gave results similar to those obtained for the undoped Tl compound. The role of Cr and V in these materials is discussed in terms of the electrical and magnetic measurements performed. Additionally, measurements of the resistance versus temperature and applied d.c. field may help to elucidate the behaviour of the irreversibility line in these Tl compounds.

Keywords: bulk superconductors; thallium; irreversibility line

After the Tl-Ba-Ca-Cu-O superconducting system was discovered^{1,2} two series of superconducting compounds were rapidly identified: Tl₂Ba₂Ca_{n-1}Cu_nO_{2n+4} with a double Tl-O layer³ and Tl₁Ba₂Ca_{n-1}Cu_nO_{2n+3} with a single Tl-O layer⁴.

Despite the fact that the absence of an orthorhombic-tetragonal phase transition in this system reduces the formation of microcracks, and that the oxygen stoichiometry is not as severe as in the case of Y-based materials, the preparation of these compounds is more complicated than the Y and Bi systems, producing a superconducting system whose potential applications are still to be explored.

In this work we have determined the inductive critical current density from the susceptibility results and we have also measured the broadening of the resistive transition in the presence of an applied d.c. magnetic field.

Our measurements are also expected to contribute to the elucidation of the irreversibility line in these materials. The irreversibility line that was first observed in magnetization measurements⁵ separates the (*H*, *T*) plane into two regions. Below this line, irreversibility is found in the magnetization while above the line the superconductor finds itself in a thermodynamic reversible state. A wide variety of models have been proposed to explain the appearance of the irreversibility line, including the transition from a liquid to a glass vortex, the melting of the vortex lattice, a giant flux creep model and the thermal activation of flux flow. However, these

models do not provide a quantitative prediction for the various experimental observations nor are they easy to compare with the experimental data.

Experimental

Samples of nominal composition Tl₂Ba₂Ca₂Cu₃O_x, Cr_{0.3}Tl₁Ba₂Cu₃O_x, Cr_{0.3}Tl₂Ba₂Ca₃Cu₄O_x and V_{0.5}Tl₁Ba₂Ca₂Cu₃O_x have been prepared by a solid-state reaction. Details of the production procedure have been published elsewhere⁶.

The X-ray diffraction pattern for the undoped sample Tl₂Ba₂Ca₂Cu₃O_x can be indexed as the 2223 phase of the Tl system; i.e. the X-rays did not detect any secondary phases. The patterns for the doped samples can also be indexed with a tetragonal phase but with slightly distorted lattice parameters due to the doping. The chemistry of the substitutions, i.e. the role played by Cr and V in the compounds, is now being studied. However, it has already been found⁷ that in the Tl-Sr-Ca-Cu-O superconductor Cr basically substitutes Ca²⁺ leaving Cu and Tl, which could seem the natural elements to substitute, unchanged. Vanadium is a 3+ ion like Cr, and therefore we expect the same type of substitution.

The a.c. susceptibility, measured at 111 Hz to avoid any interference from the frequency of the line, has been determined as a function of temperature with a Lake Shore 7000 susceptometer in a.c. applied fields of 8, 80 and 800 A m⁻¹. Furthermore, the a.c. susceptibility as a function of the a.c. field amplitude has been measured at 77 K in applied fields ranging from 3 to

*Paper presented at the conference 'Critical Currents in High T_c Superconductors', 22-24 April 1992, Vienna, Austria

Fabrication of highly oriented $Tl_2Ba_2Ca_2Cu_3O_{10}$ films with T_c over 120 K by chemical deposition and Tl-diffusion

Y Q Tang, Z Z Sheng, Z Y Chen, Y F Li and D O Pederson

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

Received 19 March 1992, in final form 13 July 1992

Abstract. Superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$ films with zero-resistance temperature over 120 K have been prepared on various substrates. Precursor BaCaCuO films were deposited by spray pyrolysis at 350–400 °C followed by a short time heating at 850 °C. Thallium was incorporated by annealing the precursor films with crude TlBaCaCuO bulk pellets in a covered alumina crucible in an oxygen atmosphere at 830 °C for 30 minutes and then at 810 °C for 16 hours. X-ray diffraction showed that the final superconducting films are mainly of 2223 phase and are highly oriented with the *c*-axis perpendicular to the surface of the substrate. The critical transport current density (J_c) of the films is near 10 000 A cm⁻².

1. Introduction

The TlBaCaCuO superconducting system [1] has drawn considerable attention because of its high T_c and environmental stability. Recently, bulk $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors with zero-resistance temperature as high as 127 K were synthesized [2, 3]. Research on Tl-based superconductor thin films was also conducted by means of physical and chemical deposition methods such as thermal evaporation [4, 5], sputtering [6–13], laser ablation [14–16], electron beam [17–19], metallorganic chemical vapour deposition (MOCVD) [20–24], and sol-gel methods such as dip-coating, spin coating or spray pyrolysis [25–27]. Despite various methods used, TlBaCaCuO superconducting films are generally prepared in two ways: direct deposition with initial Tl in the composition (pseudo-one-step process) [6, 8–12, 14, 15, 17–19, 21, 23, 25], and deposition of Tl-free precursor BaCaCuO film followed by an incorporation of thallium (two-step process) [7, 13, 16, 20, 22, 24, 27]. Both processes need an *ex situ* annealing treatment in the presence of thallium vapour and oxygen. However, the highest critical current density J_c (6×10^5 A cm⁻² at 77 K) and the highest zero-resistance temperature T_c (121 K) were obtained via the pseudo-one-step process by electron beam on an SrTiO₃ substrate [19] and by sputtering on yttrium-stabilized ZrO₂ (ysz) [9] respectively. With the two step process, the reported highest T_c is 115 K for the films deposited by laser ablation [16].

Among the techniques mentioned above, the sol-gel methods are simple and inexpensive chemical techniques for fabricating superconducting films. They can also be applied to the deposition of films on large and

irregular substrates without special equipment and modification. However, until now, zero-resistance temperature of TlBaCaCuO films prepared by these techniques [25–27] is generally inferior to those via other techniques, and no J_c value has been reported. In this paper, we report the preparation of $Tl_2Ba_2Ca_2Cu_3O_{10}$ films via deposition of precursor BaCaCuO films by spray pyrolysis followed by introduction of thallium through an annealing procedure (two-step process). The films have zero-resistance temperature up to 121 K, which is at present the highest T_c achieved by either the spray pyrolysis method or the two-step process. Moreover, the films are highly oriented with *c* axes perpendicular to the substrates and a J_c value of about 10 000 A cm⁻².

2. Experimental details

The BaCaCuO precursor films were prepared by spraying a solution on the substrates using a commercial ultrasonic humidifier (made by Holmer). The spray BaCaCu-bearing solutions were prepared by dissolving high purity Ba(NO₃)₂, Ca(NO₃)₂, and Cu(NO₃)₂ in deionized water. A ratio of Ba:Ca:Cu = 2:2.3:3 was used for most of the experiments. The total concentration of metallic ions was about 0.3 M. Figure 1 illustrates the apparatus used for aerosol generation and film deposition. The ultrasonic humidifier was modified by adding a custom-made solution chamber with a base of polyethylene membrane in order to avoid corrosion of the piezocrystal by the solution and to reduce the volume of solution needed. The very fine and uniform

Materials Research Bulletin, v 27, Issue 9, p 1049-1055, 1992

NEW THALLIUM-LEAD BASED LAYERED CUPRATES
AND THEIR SUPERCONDUCTIVITY

Z.Y.Chen*, Y.Q.Tang**, Y.F.Li, D.O.Pederson, and Z.Z.Sheng
Department of Physics, University of Arkansas
Fayetteville, Arkansas 72701, USA

(Received July 10, 1992; Communicated by A. Wold)

ABSTRACT

A new series of 1222-type (Tl,Pb)-based layered cuprate compounds $(\text{Tl,Pb})\text{Sr}_2(\text{Nd,Ce})_2\text{Cu}_2\text{O}_z$ have been successfully synthesized in the pure form and identified by powder X-ray diffraction analyses. The structure of the compounds is directly related to that of Nb-1222 $\text{NbSr}_2(\text{Nd,Ce})_2\text{Cu}_2\text{O}_z$ with tetragonal body-center lattice. The lattice parameters are $a = 3.855 \text{ \AA}$, $c = 29.47 \text{ \AA}$ for $(\text{Tl}_{0.7}\text{Pb}_{0.3})\text{Sr}_2(\text{Nd}_{0.5}\text{Ce}_{0.5})_2\text{Cu}_2\text{O}_z$, and $a = 3.853 \text{ \AA}$, $c = 29.61 \text{ \AA}$ for $(\text{Tl}_{0.7}\text{Pb}_{0.3})\text{Sr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$. Resistance measurements showed that $(\text{Tl}_{1-x}\text{Pb}_x)\text{Sr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$ ($x \leq 0.6$) prepared by the typical procedure exhibit superconductivity with $T_c(\text{onset})$ in the range 30-40 K.

MATERIALS INDEX: Thallium, Lead, Strontium, Neodymium, Cerium, Cuprate, Superconductor

Introduction

Li et al. (1,2) reported the synthesis and possible superconductivity of a new series of Ta-1222 type layered cuprates $\text{MSr}_2(\text{Ln,R})_2\text{Cu}_2\text{O}_y$ ($M = \text{Ta, Nb, Ti}$; $\text{Ln} = \text{Nd, Pr}$; $R = \text{Ce, Th}$) by considering the replacement of LaO by La_2O_2 double layers in $\text{LaBa}_2\text{Cu}_2\text{TaO}_y$ prepared by Murayama *et al.* (3). The structure of these compounds is directly related to that of $(\text{Pb,Cu})\text{Sr}_2(\text{Ln,Ce})_2\text{Cu}_2\text{O}_y$ (Pb-1222) (4), $\text{TlBa}_2\text{Ln}_2\text{Cu}_2\text{O}_y$ (Tl-1222) (5) and $(\text{Ln,Ce})_2(\text{Ln,Ba})_2\text{Cu}_3\text{O}_y$ (Cu-1222) (6) with M occupying the Pb, Tl or Cu site. Soon after the discovery of Nb-1222 compound, Cava *et al.* reported superconductivity with a T_c of 28 K for $\text{NbSr}_2(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_{10}$ (7). However, the preparation condition is very strict (7). Recently, we successfully synthesized a new Tl-based 1222-type layered cuprate

* Permanent address: Dept. of Appl. Chem., Univ. of Sci. & Technol. of China, Hefei, Anhui, 230026, China

**Permanent address: Analysis & Research Center, East China Inst. of Chem. Technol., Shanghai, 200237, China



EFFECTS OF F-DOPING AND Cl-DOPING ON FORMATION AND SUPERCONDUCTIVITY OF THE 1212-TYPE PHASE $TlSr_2CaCu_2O_{7-x}A_x$

Z. Y. Chen*, Z. Z. Sheng, Y. Q. Tang**, Y. F. Li, and D. O. Pederson

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

* Permanent address: Dept. of Appl. Chem., Univ. of Sci. & Tech. of China, Hefe, Anhui, 230026, China.

** Permanent address: Analysis & Research Center, East China Inst. of Chem. Tech., Shanghai, 200237, China.

(Received 3 May 1992 by A.A. Maradudin)

F- and Cl- substituted $TlSr_2CaCu_2O_{7-x}A_x$ ($A = F$ or Cl) have been prepared and investigated by resistance and powder x-ray diffraction measurements. The F-substitution for $x \leq 1.5$ produces nearly single 1212 phase and increases T_c by up to 20 K. These results are explained in terms of the concept of formal Cu valence. Cl-substitution is not favorable for the formation of the 1212 phase. The Cl-substitution for x as low as 0.05 prevents the formation of 1212 phase. This is due to the much larger ion radius of Cl^- than that of O^{2-} . The F-substitution improves the mechanical properties of the samples and may be useful in preparing Tl-based superconductors for practical applications.

1. INTRODUCTION

Soon after the $TlBaCaCuO$ superconducting system was discovered [1,2], the $TlSrCaCuO$ system was found to be also superconducting [3-4]. In the latter system there is a 1212-type superconducting phase $TlSr_2CaCu_2O_7$, which is difficult to form and has T_c from 0 to 70 K [4-7]. A possible reason is that the formal Cu valence of $TlSr_2CaCu_2O_7$ is too high (2.5+) [8,9]. Substitutions with metallic elements of higher valences decrease formal valence of Cu, and thus can stabilize the 1212 phase and improve its superconducting behavior [5,6,8-20]. For example, we have completed the synthesis of all derivatives of $TlSr_2CaCu_2O_7$ from substitutions of Pb for Tl, La for Sr, and Y for Ca [8]. In the framework of the formal valence of Cu, substitution of a lower valence anion, for example, F⁻ or Cl⁻, for O²⁻ would have a similar effect as the cation substitutions [9,21]. Both substitutions decrease the formal valence of Cu. In order to examine this idea, we carried out various F- or Cl- substitution experiments. In this paper, we describe the preparation of various samples and present the results from resistance and powder x-ray diffraction measurements. We also discuss the effects of F-doping and Cl-doping on the formation and superconductivity of the 1212 phase.

2. EXPERIMENTAL

The samples with nominal composition $TlSr_2CaCu_2O_{7-x}A_x$ ($A = F$, $x = 0-2.0$; or $A = Cl$, $x = 0-0.5$) were prepared using high-purity Tl_2O_3 , SrO, CaO, and SrF₂ or anhydrous CaCl₂. Appropriate amounts of SrO, CaO, and SrF₂ or anhydrous CaCl₂ were completely mixed and ground, and heated at 900-1000 °C in air for about 24 hours with several intermediate grinding to obtain uniform powders. Appropriate amounts of the

powders and Tl_2O_3 were completely mixed and ground, and pressed into pellets with a diameter of 7 mm and a thickness of 2-3 mm. The pellets were placed in a covered alumina crucible, and introduced into a preheated tube-furnace and heated to 950-1000 °C in a flowing oxygen atmosphere for 10-30 min, followed by quenching in air. Some samples were kept in the furnace and cooled naturally down to room temperature. The resistances of the samples were measured by the typical four-probe technique with an AC frequency of 27 Hz. The samples contacts were made with silver paste. The AC susceptibility (500 Hz) was measured using the mutual inductance technique. All measurements were carried out in a commercial APD closed-cycle refrigerator with computer control and processing. Powder x-ray diffraction analyses were performed with Cu K α radiation using a DIANO DTM 1057 diffractometer.

3. RESULTS

To obtain nearly single-1212 phase samples with good superconducting behavior, we carried out a series of experiments with the un-doped $TlSrCaCuO$ samples. The results showed that the formation and superconductivity of $TlSr_2CaCu_2O_7$ depended strongly on the preparation condition. Figure 1 shows the temperature-dependence of resistance for the sample of nominal composition $TlSr_2CaCu_2O_7$ prepared under different conditions. It can be seen that heating at 980-1000 °C in flowing oxygen for 10-30 minutes followed by quenching in air produced the samples with the best superconducting behavior with a zero-resistance temperature of 30-35 K. Powder x-ray diffraction showed that these samples were nearly single 1212 phase. This preparation condition was used in the

Computer-controlled thermoelectric power measurement for bulk high T_c superconductors

Y. Xin, D. Ford, and Z. Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 15 May 1991; accepted for publication 12 December 1991)

We have established a quick and easy, modified dc method to measure thermoelectric power for bulk high transition-temperature (T_c) superconductors. The temperature range investigated is from 300 to 50 K. The apparatus was developed on the basis of our already-existing commercial APD (APD CRYOGENICS INC, Allentown, Pennsylvania) superconductor characterization cryostat with a limited amount of extra instrumentation. The thermoelectric power is measured continuously within the temperature range by the control of a computer, a real time Seebeck coefficient $S(T)$ versus temperature curve is plotted on the computer screen during the measurement, and the data can be saved to a disk. The entire processing period for each sample takes less than 2 h. This apparatus was calibrated with pure lead. By measuring on high T_c superconductors which are well known in thermoelectric power, the system has been shown to have high accuracy and reliability.

I. INTRODUCTION

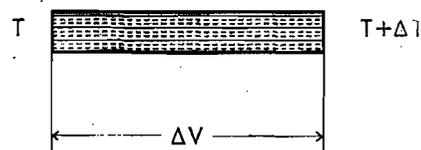
The investigation of the thermoelectric power (TEP) of high transition temperature (T_c) superconductors can yield valuable information about their electronic and structural properties. The direct result of TEP measurement is the Seebeck coefficient S , which is useful for the interpretation of the electron transport processes and interaction mechanisms in solid materials. We have constructed an apparatus suited to measuring the TEP of high T_c bulk ceramic superconductors.

If a small temperature difference, ΔT , is applied across a conductor [see Fig. 1(a)], then the negative of the derivative, $\approx -\Delta V/\Delta T$, defines the absolute thermoelectric power S (Seebeck potential) of the conductor concerned at temperature T . In a real measurement circuit [Fig. 1(b)], the voltage difference ΔV is the total contribution from both the specimen and the leads, i.e., $-\Delta V = (S - S')\Delta T$. So S equals $-(\Delta V/\Delta T - S')$. Hence the TEP measurement, if the S' is known, can be achieved by measuring the electrical voltage ΔV across a specimen, the temperature T of the specimen, and the corresponding temperature difference ΔT between the two ends of the specimen simultaneously. The method of TEP measurement based on the above principle is known as the differential method.

In practice, the thermal fluctuation and spurious potentials caused by the contact of the specimen with the substrate, the electrical leads, and the thermal detectors, can effect significantly the measured TEP results. To reduce thermal fluctuations, the conventional method is performed at constant temperatures which, by its very nature, can be a time-consuming process. To overcome the spurious potential problem, a slow ac method has been employed frequently.^{1,2} The slow ac method heats the two junctions alternatively and must wait for thermal equilibrium at a certain temperature before each measurement, therefore the method almost doubles the period for obtain-

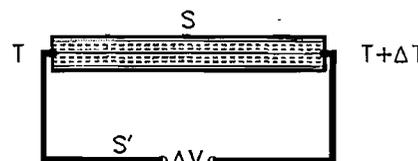
ing a datum at a given temperature. This makes the measurement time that much longer.

Being aware of such difficulties, the concept of a differential ac system for measuring TEP of metals by periodically heating the junction held at variable temperature, was initiated by two groups of researchers.^{3,4} Following that concept, several rapid ac TEP experiments were set up.^{5,6} Unfortunately these above mentioned rapid ac TEP experiment techniques are not ideal for bulk high T_c superconductors. In these techniques the temperature gradi-



$$S = -\frac{\Delta V}{\Delta T} \quad (\Delta T \rightarrow 0)$$

(a)



$$S - S' = -\frac{\Delta V}{\Delta T} \quad (\Delta T \rightarrow 0)$$

(b)

FIG. 1. (a) The definition of absolute thermoelectric power of a conductor. (b) Schematic diagram of a TEP measurement circuit.

New 100 K $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ superconducting films

Y. Q. Tang,^{a)} Z. Z. Sheng, Z. Y. Chen,^{b)} Y. F. Li, and D. O. Pederson
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 2 March 1992; accepted for publication 21 April 1992)

New $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ superconducting films on $\text{MgO}(100)$ substrates have been prepared and characterized. The superconducting films were fabricated via a two-step process. Precursor SrCaCrCuO films were first deposited by spray pyrolysis at temperature of 350–400 °C, and thallium was then incorporated by heating the precursor films between unfired TlSrCaCrCuO bulk pellets at 880–900 °C in an oxygen atmosphere. The films were then cooled down to room temperature in an oxygen or argon atmosphere. The superconducting films were single 1212 phase with c -axis perpendicular to the surface of the $\text{MgO}(100)$ substrates. Onset temperatures up to 110 K and zero-resistance temperatures up to 100 K were achieved. The critical transport currents (J_c) of the films were about $7 \times 10^3 \text{ A/cm}^2$ at 77 K.

Following the discovery of the 120 K TlBaCaCuO superconducting system,^{1,2} the TlSrCaCuO system was found also to be superconducting at 70–80 K.^{3,4} In the latter system, there is a 1212-type phase $\text{TlSr}_2\text{CaCu}_2\text{O}_7$, which is difficult to synthesize in the pure form, and is often not superconducting.^{5,6} When the 1212 phase is subjected to elemental substitutions, for example, Pb for Tl (Refs. 5 and 7) or R (rare earths) for Ca,^{8,9} it is formed easily. The superconducting transition temperature is improved significantly, usually to a T_c of 75–90 K.^{5,7–9} Recently, we discovered a new 1212-type phase, the Cr-substituted $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$, which exhibits T_c as high as 110 K and forms easily.¹⁰ Motivated by its easy formation and high T_c , we have prepared $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ superconducting films. In this letter, we report for the first time the preparation and characterization of single 1212 phase $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ superconducting films on $\text{MgO}(100)$ substrates. The films were prepared via a two-step process involving the deposition of precursor films by spray pyrolysis and the thallium incorporation by post-annealing. Zero-resistance temperatures of the films were as high as 100 K, and the critical transport current density (J_c) was about $7 \times 10^3 \text{ A/cm}^2$ at 77 K.

The solutions used for spray pyrolysis deposition were prepared by dissolving analytical grade CrO_3 , $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ into deionized water. Two different starting compositions, $\text{Cr}_{0.2}\text{Sr}_2\text{CaCu}_{1.5}(\text{NO}_3)_x$ and $\text{Cr}_{0.2}\text{Sr}_2\text{CaCu}_2(\text{NO}_3)_x$ were used. The total concentration of metallic ions in the solutions was about 0.3 M. A modified commercial ultrasonic humidifier (made by Holmer) was used to generate very fine and uniform mists. The mists were carried by oxygen flow onto a $\text{MgO}(100)$ substrate heated by a hot plate to 350–400 °C, resulting a film layer. The as-deposited precursor films were then put between unfired $\text{TlCr}_{0.2}\text{Sr}_2\text{CaCu}_{1.5-2}\text{O}_x$ bulk pellets in a covered alumina crucible, and were heated in a programmable tube furnace at 830–900 °C under an oxygen atmosphere. The starting Sr:Ca:Cr:Cu ratio of the bulk pellets was the

same as that of the precursor films being annealed. An argon atmosphere was also used in the cooling step for some films in order to improve their superconducting properties. The film thickness was measured using a Sloan Dektak surface profilometer, and film morphology was investigated using an ISI 40 scanning electron microscope (SEM). X-ray diffraction patterns were obtained using a DIAMO DIM 1057 diffractometer with $\text{Cu } K\alpha$ radiation. The ac resistances (27 Hz) of the films were measured by the standard four-probe technique with silver paste contacts. The measurements were carried out in a commercial APD closed-cycle refrigerator in the temperature range from 50 to 300 K. Data collection and data processing were carried out on an IBM-PC computer. J_c was determined by measuring the current-voltage curve using the four-probe technique (in the standard Hall bar configuration) at 77 K in liquid nitrogen.

The as-deposited precursor films showed a light brown color and were not conducting. After the Tl-processing procedure, the films turned black, and were superconducting. A typical room-temperature resistivity of these films was about 1 m Ω cm. The thicknesses of the films ranged from 0.7 to 1.5 μm . Figure 1 shows photographs of an as-deposited precursor film and a processed superconducting $\text{TlSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$ film. The precursor film showed a noncrystal appearance, whereas the superconducting film consists of uniform crystalline grains with an average size of 3 μm . Under the typical deposition condition, the composition of metallic atoms in the precursor films would be the same as that in the solutions. Since the precursor films are annealed with the corresponding bulk pellets, the final composition in the superconducting films is expected to be about the same as that in the bulk pellets, which have been examined by electron microanalysis.¹⁰

Table I lists preparation condition and T_c for some films. The preparation condition of the TlSrCaCrCuO films was much less sensitive than that for TlBaCaCuO superconducting films. Zero-resistance temperatures above 95 K were easily obtained for a wide range of conditions.

Figure 2 shows resistance-temperature curves of the films deposited from the solution $\text{Cr}_{0.2}\text{Sr}_2\text{CaCu}_{1.5}(\text{NO}_3)_x$ and annealed at different temperatures. Curves a, b, and c represent the films annealed at 830, 870, and 880 °C, re-

^{a)}Permanent address: Analysis & Research Center, East China Institute of Chemical Technical, Shanghai, 200237, People's Republic of China.

^{b)}Permanent address: Department of Appl. Chem., Univ. of Sci. & Tech. of China, Hefei, Anhui, 230026, People's Republic of China.



A NEW SUPERCONDUCTING 1201-TYPE PHASE $(\text{Ti,Cr})\text{Sr}_2\text{CuO}_5$

Z.Z.Sheng, Y.F.Li, Y.Q.Tang, Z.Y.Chen, and D.O.Pederson

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

(Received 17 March 1992 by A. A. Maradudin)

(accepted for publication 18 May 1992)

A new 1201-type phase $(\text{Ti,Cr})\text{Sr}_2\text{CuO}_5$ has been synthesized and identified. This phase has a tetragonal unit cell (space group $P4/mmm$) with $a = 3.795 \text{ \AA}$ and $c = 8.880 \text{ \AA}$, and is superconducting at 40-50 K. Cr in $(\text{Ti,Cr})\text{Sr}_2\text{CuO}_5$ plays a similar role to Pb in $(\text{Ti,Pb})\text{Sr}_2\text{CuO}_5$, which is instructive in the search for new Cr-based superconductors.

Observation of superconductivity in the TiSrCuO system was sought immediately after the discovery of the TiBaCuO superconducting system^{1,2}. However, the TiSrCuO system is not superconducting although it has low room-temperature resistivity and shows a metallic resistance-temperature behavior³. When doped by a rare earth (R) or Pb, the TiSrCuO system shows superconductivity around 40-50 K and even 80-90 K⁴⁻⁷. A 1201 phase $\text{Ti}(\text{Sr,R})_2\text{CuO}_5$ or $(\text{Ti,Pb})\text{Sr}_2\text{CuO}_5$ is responsible for the 40-50 K superconductivity⁴⁻⁷, whereas a 1212 phase $\text{TiSr}_2(\text{Sr,R})\text{Cu}_2\text{O}_7$ is responsible for the 80-90 K superconductivity^{7,8}. Recently, we reported a new 1212-type phase, the Cr-substituted $\text{TiSr}_2(\text{Ca,Cr})\text{Cu}_2\text{O}_7$, which exhibits T_c up to 110 K⁹. This is the first time that a single-element substitution for $\text{TiSr}_2\text{CaCu}_2\text{O}_7$ enhances the T_c of the 1212-phase to above 100 K. Motivated by the great capability of the 3d-element Cr in forming superconducting phases and enhancing T_c , a further series of substitution experiments of Cr for the Ca-free TiSrCuO system was carried out. It turns out that the Cr-substituted TiCrSrCuO system is also superconducting at 40-50 K and at 77 K. In this communication, we report the preparation and identification of the 40-K phase which is a 1201-type phase $(\text{Ti,Cr})\text{Sr}_2\text{CuO}_5$. The identification for the 77-K phase will be reported elsewhere.

The TiCrSrCuO samples were prepared using high-purity oxides, Ti_2O_3 , Cr_2O_3 , SrO , and CuO , by the solid state reaction method. A typical procedure is as follows. Appropriate amounts of component oxides were completely mixed and ground, and pressed into pellets with a diameter of 7 mm and a thickness of 2-3 mm. The pellets were placed in a covered alumina crucible. The crucible with the contents was introduced into a preheated tube furnace, and heated at 950-1000 °C in flowing oxygen for 5-30 minutes, followed by quenching. The resulting samples were examined by resistance and AC susceptibility measurements and by powder x-ray diffraction analyses. AC resistance (27 Hz) was measured by the standard four-probe technique with

silver paste contacts. AC susceptibility (500 Hz) was measured using the mutual inductance technique. All measurements were carried out in a commercial APD closed-cycle refrigerator system with computer control and processing. Powder x-ray diffraction analyses were carried out with $\text{Cu-K}\alpha$ radiation using a DIANO DTM 1057 diffractometer.

Figure 1 shows resistance-temperature curves for nominal samples $(\text{Ti}_{0.5}\text{Cr}_{0.5})\text{Sr}_2\text{CuO}_5$ prepared by heating at 800, 850, 900, 950 and 1000 °C for 15 minutes in flowing O_2 followed by quenching. All samples are superconducting, and the sample prepared at 950 °C exhibits the best superconducting behavior with an onset temperature of 50 K and a zero-resistance temperature of 40 K. AC susceptibility measurements showed superconducting transition temperatures similar to those by resistance measurements. As an example, Figure 2 shows the temperature-dependence of resistance and ac

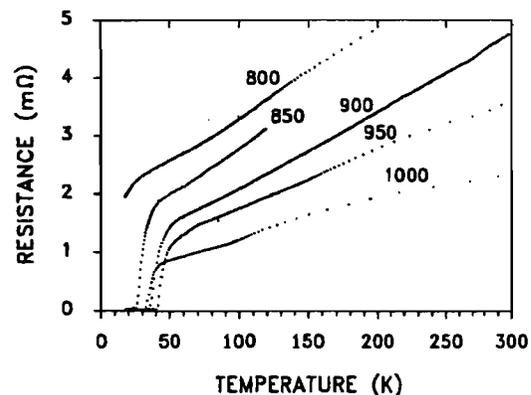


Figure 1 Resistance-temperature curves for nominal samples $(\text{Ti}_{0.5}\text{Cr}_{0.5})\text{Sr}_2\text{CuO}_5$ prepared at different temperatures.

Effect of a bias field (up to 1 T) on the a.c. susceptibility of $\text{Cr}_{0.3}\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ *

J.S. Muñoz, M. Pont, T. Puig, Z.Z. Sheng†, Y. Xin†, D.X. Gun† and D.O. Pederson†

Grup d'Electromagnetisme, Dept. de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

† Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

The a.c. susceptibility of bulk $\text{Cr}_{0.3}\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ at 8 A m^{-1} and 111 Hz has been measured as a function of temperature and d.c. bias field ranging from 0 to $795\,000 \text{ A m}^{-1}$. As the d.c. magnetic field is increased a decrease in the critical temperature as well as in the temperature at which the imaginary part of the susceptibility peaks is observed. We have also measured the a.c. susceptibility as a function of a.c. magnetic field amplitude without d.c. bias field. In this case no decrease in the transition temperature is observed despite the decrease found again in the temperature at which the imaginary component of the susceptibility has its maximum. The peak temperature, from the d.c. bias field measurements, has been related to the irreversibility line obtained from the broadening of the resistive transition under the presence of a d.c. magnetic field.

Keywords: critical currents; bias field; a.c. susceptibility

The study of the dynamics of flux lines in high temperature superconductors (HTS) is a subject of considerable interest to understand the mechanisms involved in it. Furthermore, these mechanisms seem to be intimately related, adding further difficulty to the interpretation of the different experimental measurements. Moreover, the weak electronic coupling between CuO_2 layers in Bi and Tl compounds, the short coherence length and the high value of the Ginzburg Landau κ results in an unusual mobility of the flux lines, thus reducing the expected high critical current. In particular, the irreversibility line and the type of transition associated with it (liquid to glass vortex state^{1,2}, melting of the lattice³⁻⁵, thermal activated depinning processes^{6,7}) have attracted considerable attention. There are several methods that have been widely used to determine the irreversibility line since the work of Müller *et al.*⁸ where the ZFC and FC $M(T)$ in a constant field were measured. It has also been found that the measured $T_{ir}(H)$ strongly correlates with hysteresis⁹. Isothermal measurements of $M(H)$ have been investigated in an attempt to determine $H_{ir}(T)$ ¹⁰. The resistivity of HTS in low and moderate magnetic fields follows an Arrhenius law on temperature, suggesting thermally activated flux motion. On the other hand the imaginary component of the a.c. susceptibility peaks at a frequency given by $\omega = \omega_0 \exp(-U/k_B T)$ where the

activation energy U appears consistent with that found in resistivity measurements and the prefactor ω_0 seems to be field independent¹¹.

However, the results obtained by the different methods show some disagreement even for the same system. In order to try to clarify these problems we have measured the a.c. susceptibility of a Tl based compound in the presence of a d.c. bias field.

Experimental method

Cr substitution in the Tl-1212 phase was seen to enhance T_c , producing high quality samples so that Cr was then added to the 1223 phase, giving the nominal composition $\text{Cr}_{0.3}\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. This was done not only to enhance T_c but also because it is easy to prepare and to obtain a very good quality material for many possible applications. The details of the sample preparation have been published elsewhere¹². From the X-ray diffraction pattern no significant amount of secondary phase was found.

We have measured the a.c. susceptibility as a function of temperature for a.c. fields ranging from 8 to 8000 A m^{-1} at 111 Hz as well as at 8 A m^{-1} with the d.c. field superimposed ranging from 0 to $795\,000 \text{ A m}^{-1}$.

The sample geometry is a thin slab with the largest dimension parallel to the applied a.c. and d.c. fields. The data have been corrected for demagnetizing effects, although the earth's magnetic field has not been shielded in any measurement.

*Paper presented at the conference 'Critical Currents in High T_c Superconductors', 22 - 24 April 1992, Vienna, Austria

Fabrication of Superconducting $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ Thin Films by Laser Ablation and Thallium Diffusion

Yongqiu TANG, Weiang LUO, Zuyao CHEN, Seifollah NASRAZADANI*, Fui T. CHAN, Gregory SALAMO, Donald O. PEDERSON and Zhengzhi SHENG

Department of Physics, The University of Arkansas, Fayetteville, Arkansas 72701, USA

(Received June 29, 1992; accepted for publication September 19, 1992)

Superconducting $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ thin films have been prepared on $\text{MgO}(100)$ substrates via laser ablation and thallium diffusion. Precursor SrCaCrCuO films were first deposited by an excimer laser; thallium was then incorporated by annealing the precursor films between un-fired TlSrCaCrCuO bulk pellets. The product superconducting films are 1212 phase and exhibit $T_c(\rho=0)$ up to 90 K and $J_c(\text{transport})$ up to 10^4 A/cm^2 .

KEYWORDS: superconducting thin film, high T_c superconductor, Tl-Sr-Ca-Cu-O system, "1212" phase, Cr addition, laser ablation

Among M-substituted ($M=\text{Pb}, \text{Bi}, \text{Cr}$ or rare earth) 1212-type phase $(\text{Tl}, \text{M})\text{Sr}_2(\text{Ca}, \text{M})\text{Cu}_2\text{O}_7$ compounds,¹⁻⁷ the Cr-substituted $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ exhibits a T_c as high as 110 K and is easy to synthesize.⁷ Motivated by this easy formation and high T_c , we have successfully prepared 100 K $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ superconducting films via spray pyrolysis and thallium diffusion.⁸ However, the films obtained by the spray technique are generally thick and rough on surface which may not be suitable for certain electronic applications. In this paper, we report the preparation of $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ superconducting films on $\text{MgO}(100)$ substrates using laser ablation and thallium diffusion. Zero-resistance temperature $T_c(\rho=0)$ of the best films was 90 K, and the critical transport current J_c was about 10^4 A/cm^2 at 77 K.

The laser ablation target with nominal composition of $\text{Cr}_{0.2}\text{Sr}_2\text{CaCu}_2\text{O}_x$ was prepared by sintering a pellet of properly mixed powder of Cr_2O_3 , SrO , CaO and CuO at 880°C for 24 h. Precursor films were deposited onto $\text{MgO}(100)$ substrates at $260\text{--}280^\circ\text{C}$ using a Kr-F excimer laser with a wavelength of 248 nm. The laser operated at 20 Hz with a power of 200 mJ. The oxygen pressure in the deposition chamber was 200 mTorr and the deposition time was 7–20 min. The as-deposited precursor films were then put between unfired $\text{TlCr}_{0.2}\text{Sr}_2\text{CaCu}_2\text{O}_x$ bulk pellets in a covered alumina cylinder, and were heated in a programmable tube-furnace at $860\text{--}880^\circ\text{C}$ for 30–180 min in an oxygen atmosphere. A high temperature worked with a short annealing time while the lower temperature treatment took longer. In the cooling step, some films were cooled in argon while others were cooled in oxygen. Different cooling rates were used. The methods and instruments used for investigating the thickness, morphology, X-ray diffraction patterns as well as the T_c and J_c of films were all described in ref. 8.

The precursor films deposited by laser ablation were mirror-like with a shiny dark brown color and were not conducting. The thickness of the films varied from 0.3–0.8 μm depending on the deposition time. After the Tl-diffusion procedure, the films turned black, and were superconducting. Although the preparation conditions for TlSrCaCrCuO films were much less sensitive than that for TlBaCaCuO superconducting films,⁸ the annealing procedure was still very crucial for the superconducting properties.

Table I lists the processing conditions and T_c and J_c for some films. It shows clearly that both annealing temperature and cooling rate play very important roles in the film properties. Film S1 was annealed at 880°C for 30 min in an oxygen flow. The X-ray diffraction pattern of this film (Fig. 1) shows that the film is single 1212 phase $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ and exhibits a strong orientation with c-axis perpendicular to the surface of the $\text{MgO}(100)$ substrate. However, $T_c(\rho=0)$ of the film is only 82 K and the J_c is also low ($< 10^3 \text{ A/cm}^2$). The SEM photograph (Fig. 2(a)) illustrates that the film consists of uniform crystalline grains with an average size of 2 μm , but the morphology is porous. Obviously, it is the porosity that causes the poor J_c of film. In contrast, films processed at lower temperature have random orientation but are more dense (Fig. 2(b)). These films exhibit higher $T_c(\rho=0)$ and J_c . By decreasing the temperature from 880°C to 865°C , T_c is increased from 82 K to 90 K (also see Fig. 3). A rapid cool-

Table I. Annealing condition and $T_c(\rho=0)$ and J_c for some films.

Sample	Annealing condition	$T_c(\text{K})$	$J_c(\text{A/cm}^2)$
S1	880°C , 30 min (O_2), cooling rate: $50^\circ\text{C}/\text{min}$ (Ar)	82	6×10^2
S2	875°C , 60 min (O_2), cooling rate: $50^\circ\text{C}/\text{min}$ (Ar)	85	1×10^3
S3	870°C , 90 min (O_2), cooling rate: $50^\circ\text{C}/\text{min}$ (Ar)	86	2×10^3
S4	870°C , 90 min (O_2), cooling rate: $50^\circ\text{C}/\text{min}$ (O_2)	87	2×10^3
S5	865°C , 150 min (O_2), cooling rate: $2^\circ\text{C}/\text{min}$ (O_2)	90	1×10^4
S6	860°C , 180 min (O_2), cooling rate: $2^\circ\text{C}/\text{min}$ (O_2)	90	1×10^4

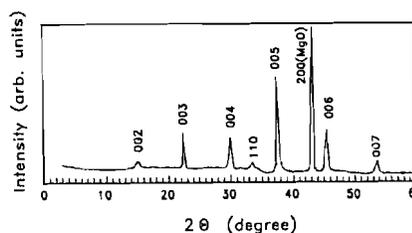


Fig. 1. X-ray diffraction pattern for the superconducting $\text{TlSr}_2(\text{Ca}, \text{Cr})\text{Cu}_2\text{O}_7$ film S1 in Table I. It shows that this film is single 1212 phase and is highly oriented.

*Department of Mechanical Engineering, The University of Arkansas.

Optimum preparation and elemental addition for Tl-based 2223 phase $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$

Y. Xin, Y.F. Li, D.X. Gu, D.O. Pederson and Z.Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 16 September 1991

TlBaCaCuO samples with 95%-pure 2223 phase $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ and 120 K T_c can be prepared in a non-closed system from component oxides with a starting composition of 2223 by heating at 895°C for about 48 h in flowing oxygen. With this procedure, elemental addition at 0.2 molar level maintains 2223 phase purity of 75-95% and a T_c of 112-120 K for most of the investigated elements (Na, K, Rb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Zn, Cd, Hg, Se and Te).

1. Introduction

$Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ holds the record of T_c of 125 K as a stable and reproducible superconductor. There have been numerous papers worldwide on the study of this compound. However, compared with the rare earth-based 123 compound and the bismuth-based 2223 phase, the study is far from sophisticated. Even the practical issue of producing high quality materials remains a challenge. Since the melting point of Tl_2O_3 is 717°C at the atmospheric pressure and beyond this point the vaporization of Tl_2O_3 is rather fast, almost all the methods reported so far are heating the samples for a short period of time from several minutes to several hours [1-14]. A few groups heat the samples for a long period of time; but at lower temperatures. For example, Adachi et al. [15] heated the samples for 240 h at below 800°C. It is obvious that with such a short time or such a low temperature the solid state reaction of the component chemicals is far from sufficient. To overcome the problem of Tl_2O_3 evaporation, many groups use prefired BaCaCuO precursor mixing with Tl_2O_3 to get the expected composition and then heat them for a short period of time [1-3, 5-14]. This method, in some degree, can improve the chemical reaction and reduce the excessive loss of thallium. However, samples with high quality and high phase purity are still hard to achieve even with precursors. With starting

composition $Tl_2Ba_2Ca_2Cu_3O_x$, the dominant phase in samples is the 2212 phase $Tl_2Ba_2CaCu_2O_{8-\delta}$ instead of 2223 phase $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ [3, 16]. Some groups reported that a non-stoichiometric starting composition (most of them using excess Ca or Cu or both) can facilitate the formation of the 2223 phase (see for example, ref. [3]). However, in this case, the excess chemicals may form some parasitic non-superconducting crystalline or become precipitate particles which will result in poor quality samples. After a systematical test for the optimum heating condition for the 2223 phase $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$, we found that once the Tl_2O_3 is participating in the formation of the superconducting structure, its vaporization becomes much slower. Therefore, we can set the heating time as long as 48 h and heating temperature as high as 895°C (slightly below the melting point of the 2223 phase) in a non-closed system. Furthermore, we use directly the metal oxides according to the composition $Tl_2Ba_2Ca_2Cu_3O_x$ as the starting materials. With this procedure, the quality of the samples is greatly improved because of sufficient reaction of the chemicals. Besides the very good superconducting properties and high phase purity, the mechanical properties such as density and hardness, are significantly improved. The density of the $Tl_2Ba_2Ca_2Cu_3O_x$ samples can be as high as 6.36 ± 0.5 g/cm³ which is about 91% of the calculated value for a perfect 2223 crystal. Moreover, we

Formation and superconductivity of 1212-type phase $\text{TlSr}_2(\text{Sr}, \text{Pr})\text{Cu}_2\text{O}_7$ and $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{Pr})\text{Cu}_2\text{O}_7$

Z Z Sheng, Y Xin, J M Meason, D X Gu and D O Pederson

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 7 February 1991

Abstract. Nominal samples $(\text{Tl}_{1-x}\text{Pb}_x)\text{Sr}_2(\text{Sr}_{1-y}\text{Pr}_y)\text{Cu}_2\text{O}_7$ were prepared, and were investigated by powder x-ray diffraction analysis and by resistance measurement. The results showed that a rare earth is required for the formation of the 1212 phase $(\text{Tl}_{1-x}\text{Pb}_x)\text{Sr}_2(\text{Sr}_{1-y}\text{Pr}_y)\text{Cu}_2\text{O}_7$. Pb doping is necessary to increase the T_c of the 1212 phase from 90 K to about 100 K. The formation and superconducting behaviour of the 1212 phase depend on both x and y . The results can be explained in the framework of the average Cu valence.

1. Introduction

The discoveries of the the 90 K Tl-Ba-Cu-O system [1, 2] and 120 K Tl-Ba-Ca-Cu-O system [3, 4] have stimulated numerous activities on the Tl-based superconductors. Two series of superconducting phases $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$ and $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$ were rapidly identified [5-8]. The member of $n=2$ with single TlO plane— $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, an analogue of the famous 123 phase $\text{YBa}_2\text{Cu}_3\text{O}_7$ —is easily subjected to elemental substitutions, forming a large family of 1212-type Tl-based superconductors with the general formula $(\text{Tl}, \text{M})(\text{A}', \text{M}')_2(\text{A}'', \text{M}'')\text{Cu}_2\text{O}_7$, where $\text{M} = \text{Pb}$ or Bi , $\text{A}' = \text{Ba}$ or Sr , $\text{M}' = \text{La}$, $\text{A}'' = \text{Ca}$ or Sr and $\text{M}'' = \text{R}$ (rare earth). The discoveries of the Ca-free $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_7$ with T_c of 90 K and $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_7$ with T_c of 100 K have added new members to the 1212 family [9-12]. We believe that more new members will be synthesized soon†. In this paper we report the effects of Pr and Pb on the formation and superconductivity of the 1212 phase $\text{TlSr}_2(\text{Sr}, \text{Pr})\text{Cu}_2\text{O}_7$ and $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{Pr})\text{Cu}_2\text{O}_7$. We present the preparation procedure of the samples and give the results from powder x-ray diffraction analysis and resistance measurement. The results are discussed according to the concept of the average Cu valence.

2. Experiment

Samples with nominal compositions of $\text{TlSr}_2(\text{Sr}_{1-y}\text{Pr}_y)\text{Cu}_2\text{O}_z$, $(\text{Tl}_{0.8}\text{Pb}_{0.2})\text{Sr}_2(\text{Sr}_{1-y}\text{Pr}_y)\text{Cu}_2\text{O}_z$

† For example, we recently discovered a new 1212-type superconductor with Cr-substituted $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ with T_c of 110 K [13].

and $(\text{Tl}_{1-x}\text{Pb}_x)\text{Sr}_2(\text{Sr}_{0.6}\text{Pr}_{0.4})\text{Cu}_2\text{O}_z$ were prepared using high-purity Tl_2O_3 , PbO_2 , SrO , Pr_6O_{11} and CuO . Component oxides with certain metallic atom ratios were completely mixed and ground. The powders were pressed into pellets with a diameter of 15 mm and a thickness of about 2 mm under a pressure of 7000 kg cm^{-2} . The pellets were placed in an Al_2O_3 tube. The opening of the tube was covered with an Al_2O_3 plug. The Al_2O_3 tube with its contents was then put into a preheated tube furnace and heated at about 1000°C in flowing oxygen for 30 minutes, followed by furnace cooling to below 200°C . It should be noted that the Tl in the starting compositions was about 20% more than the 1212 stoichiometry. The excessive Tl was used to compensate for the Tl loss during heating so that the metallic atom ratios in the resultant samples could be nearly 1:2:1:2 [(Tl, Pb):Sr:(Sr, Pr):Cu]. The resultant samples were examined by powder x-ray diffraction analyses and by resistance measurements (ΔC , 27 Hz). Powder x-ray diffraction was carried out with $\text{Cu K}\alpha$ radiation using a DIANO DIM 1057 diffractometer. Resistance (ΔC , 27 Hz) was measured by the standard four-probe technique with silver paste contacts. All measurements were made with computer control and processing, and were carried out in a commercial APD refrigerator.

3. Results

The diffraction lines of most of the samples could be assigned to a 1212 phase and/or a 1201 phase [(Tl, Pb) : Sr : (Sr, Pr) : Cu]. As an example, Figure 1 shows the powder x-ray diffraction patterns for nominal

Comparison of Pb, Pb-Sb, Pb-V, Pb-Mo and Pb-W substituted Bi-Sr-Ca-Cu-O

Y. Xin and Z.Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

S. Nasrazadani

Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701, USA

Received 31 August 1990

Revised manuscript received 7 February 1991

Nominal samples $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{M}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and $\text{Bi}_{1.3}\text{Pb}_{0.3}\text{M}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, where M = Pb, Sb, V, Mo and W, were synthesized and investigated by resistance, AC susceptibility, and powder X-ray diffraction measurements. The morphology of some samples was also studied using scanning electron microscope. The results show that in all the $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{M}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples, the 2223 phase is increased; in the $\text{Bi}_{1.3}\text{Pb}_{0.3}\text{M}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples, Pb, Pb-V, or Pb-Mo substituted can greatly enhance the 2223 phase, but Pb-Sb or Pb-W substitution causes degeneration in superconductivity. The substitute(s) is believed to be incorporated into the crystalline structure, rather than simply acting as a flux in growth of the high- T_c phase.

1. Introduction

Following the discovery of high- T_c superconductivity in the Bi-Sr-Ca-Cu-O system [1], a great number of studies on this system were carried out. A series of superconducting phases of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ with $n=1$ (2201 phase, $T_c < 20$ K), 2 (2212 phase, $T_c = 85$ K) and 3 (2223 phase, $T_c = 110$ K) were identified [2-4]. Unfortunately, the 2223 phase with the highest T_c is extremely difficult to prepare in a pure form since it usually intergrows with the 2212 phase. Numerous efforts have been made to enhance the 2223 phase by adjusting thermal treatment [5-8], modification of the starting composition [9-11] and by elemental substitution. A very important point is that partial substitution of Pb for Bi in this system enhances the 2223 phase [12-15]. Recently, Pb-Sb has most often been used for the substitution since zero resistance at 133 K in the Pb-Sb substituted Bi-Sr-Ca-Cu-O system was reported [16,17]. Substitution experiments with alkaline metal [18], Cd [19], Y [20], V [21], Ag and Nb [22] were also reported.

In attempts to find some other suitable substitutes

to enhance 2223 phase in Bi-Sr-Ca-Cu-O and to understand the function of the substitutions in the system, we have carried out extensive elemental substitution experiments on Bi-Sr-Ca-Cu-O system. In this paper, we report the results of the substitution of Pb-V, Pb-Mo and Pb-W for Bi in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, compared with Pb and Pb-Sb substitution. We chose Pb-M double substitution because: 1) Pb had been proved a successful substitute, 2) the charge carrier concentration resulting from Pb-M substitution might be different from that for Pb single substitution, 3) we wanted to compare this system with the quite popular Pb-Sb substitution. We prepared two series of samples with nominal compositions of $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{M}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and $\text{Bi}_{1.3}\text{Pb}_{0.3}\text{M}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, where M = Pb, Sb, V, Mo, or W, and examined them by resistance, AC susceptibility measurements and powder X-ray diffraction analyses. Scanning electron microscope (SEM) was used to study the morphology of samples $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and $\text{Bi}_{1.3}\text{Pb}_{0.3}\text{M}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. The results showed that Pb-V and Pb-Mo, as well as Pb, are good substitutes to enhance the high- T_c phase. Samples with about 90% 2223 phase and zero-

PENETRATION DEPTH MEASUREMENTS OF THE HIGH- T_c SUPERCONDUCTORS VIA ELECTRON PARAMAGNETIC RESONANCE

B. Rakvin^{a)}, T.A. Mahl, A.S. Bhalla^{b)}, Z.Z. Sheng^{c)}
and N.S. Dalal

Department of Chemistry, West Virginia University
Morgantown WV 26506-6045

(Received September 25, 1989; in final form October 10, 1989)

Abstract Electron Paramagnetic Resonance (EPR) has been found to be a quick and easily accessible method for measuring the London penetration depth, λ , for the high- T_c superconductors. The method utilizes the broadening of the EPR signal of a spin-probe compound adsorbed to the surface of the superconductor. The broadening of the EPR signal is due to the formation of the magnetic flux lattice below T_c and is measured as the second moment, $\langle \Delta H^2 \rangle$. $\langle \Delta H^2 \rangle$ is fitted to the Brandt equation for a simple triangular lattice: $\langle \Delta H^2 \rangle = 0.00371 \lambda_0 [1 - (T/T_c)^4]^{-1/2}$. This method yields $\lambda_0 = 2700 \pm 100$ Å with a T_c of 84 K for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and 2520 ± 100 Å with a T_c of 119 K for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. The precision of ± 100 Å or better compares well with those of the more traditional techniques of $\mu^+\text{SR}$, neutron diffraction, and magnetic susceptibility.

INTRODUCTION

Although other methods are used for the measurement of λ , such as muon spin resonance ($\mu^+\text{SR}$)^{1,2}, d.c. susceptibility^{3,4}, neutron scattering⁵, and NMR^{6,7}, the procedure based on EPR spin-probe methodology was thought to be desirable, because each of these methods has some shortcomings¹⁻⁶. For example, muon spin resonance measures λ via line broadening as a result of the flux penetration. However, one must estimate the contribution from relaxation broadening, which appears hard to do^{1,2}. Neutron scattering needs access to a high (neutron) flux reactor and studies the bulk properties of a sample⁵. Susceptibility measurements require an

Semiconducting $\text{TlSr}_2\text{RCu}_2\text{O}_7$ (R = rare earth) and its superconducting derivatives

Z. Sheng, Y. Xin, D.X. Gu, J.M. Meason, J. Bennett, D. Ford, and D.O. Pederson

Department of Physics, University of Arkansas, 105 Physics Building, Fayetteville, AR 72701, USA

Received March 28, 1991

Semiconducting $\text{TlSr}_2\text{RCu}_2\text{O}_7$ (R=Pr or Er) with a 1212-type structure has been synthesized in the single-phase form. Partial substitution of Sr^{2+} for R^{3+} converts the semiconductor to a 90 K superconductor $\text{TlSr}_2(\text{R}_{1-x}\text{Sr}_x)\text{Cu}_2\text{O}_7$. A combination substitution, Sr^{2+} for R^{3+} and Pb^{4+} for Tl^{3+} , leads to the Ca-free 100 K superconductor $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{R}, \text{Sr})\text{Cu}_2\text{O}_7$. The results are obtained in the framework of the mixed $\text{Cu}^{2+}/\text{Cu}^{3+}$ valence.

Introduction

The discoveries of the 90 K TlBaCuO and 120 K TlBa_2CuO systems [1-4] have led to a number of new Tl-based superconducting systems. Among them is the TlSrCaCuO system [5]. When a rare earth (R) is introduced into this system, the TlSrCaRCuO system exhibits superconductivity at about 90 K [6]. The phase responsible for the superconductivity is $\text{TlSr}_2(\text{Ca}, \text{R})\text{Cu}_2\text{O}_7$ (1212 phase) [7]. Meanwhile, other 1212-type Tl-based superconductors $(\text{Tl}, \text{M})\text{Sr}_2\text{CaCu}_2\text{O}_7$ and $(\text{Tl}, \text{M})\text{Sr}_2(\text{Ca}, \text{R})\text{Cu}_2\text{O}_7$ with $\text{M} = \text{Pb}$ or/and Bi were also reported [8, 9]. Further work showed that when R is added to the TlSrCaCuO system, the Ca-free TlSrRCuO system is superconducting up to about 90 K [12, 13], and the phase responsible for the 90 K superconductivity is also a 1212-type compound $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_7$ [13]. From the point of view of the R-substitution, therefore, the compound $\text{TlSr}_2\text{SrCu}_2\text{O}_7$ would be synthesized. After many efforts, however, we were unable to prepare the 1212-type compound $\text{TlSr}_2\text{SrCu}_2\text{O}_7$, instead, we did successfully synthesize single phase 1212-type $\text{TlSr}_2\text{RCu}_2\text{O}_7$, which is a semiconductor. It turned out that Sr-substitution for R in the semiconducting $\text{TlSr}_2\text{RCu}_2\text{O}_7$ produced the 90 K superconducting $\text{TlSr}_2(\text{R}, \text{Sr})\text{Cu}_2\text{O}_7$. In this paper, we report the synthesis and identification of the semiconductor $\text{TlSr}_2\text{RCu}_2\text{O}_7$ (R=Pr or Er). We give its superconducting derivatives $\text{TlSr}_2(\text{R}_{1-x}\text{Sr}_x)\text{Cu}_2\text{O}_7$ and $(\text{Tl}_{1-x}\text{Pb}_x)\text{Sr}_2(\text{R}_{1-x}\text{Sr}_x)$

Cu_2O_7 . The latter is the first Ca-free superconductor with T_c above 100 K [14, 15]. The results are discussed in terms of the concept of the mixed Cu valence.

2. Experimental

The samples were prepared using high-purity oxides Tl_2O_3 , SrO , Pr_6O_{11} , Er_2O_3 , and CuO . In a typical procedure, component oxides with a certain metallic atom ratio were completely mixed and ground. The powder was pressed into a pellet with a diameter of 15 mm and a thickness of about 2 mm under a pressure of 7,000 kg/cm^2 . The pellet was placed in an alumina tube. The opening of the tube was covered with an alumina plug. The alumina tube with contents was then put into a preheated tube furnace, and heated at about 1000 °C in flowing oxygen for 30 min., followed by furnace cooling to below 200 °C. Note that in the present experiments, Tl in starting compositions is in excess by 20% over the 1212 stoichiometry in order to compensate the Tl loss during heating. The resultant samples were examined by resistance measurements and by powder x-ray diffraction analyses. Resistance (ac, 27 Hz) was measured by the standard four-probe technique with silver paste contacts. All measurements were made with computer control and processing and were carried out in a commercial APD closed cycle refrigerator. Powder x-ray diffraction was carried out with $\text{Cu-K}\alpha$ radiation with use of a DIANO DIM 1057 diffractometer.

3. Results

Single phase sample was synthesized for both $\text{TlSr}_2\text{PrCu}_2\text{O}_7$ and $\text{TlSr}_2\text{ErCu}_2\text{O}_7$. The powder x-ray diffraction pattern for $\text{TlSr}_2\text{PrCu}_2\text{O}_7$ could be indexed based on a tetragonal structure with unit cell of $a = 3.845(1)$ Å and $c = 12.098(2)$ Å. Similarly, the diffraction pattern for $\text{TlSr}_2\text{ErCu}_2\text{O}_7$ could be indexed as a tetragonal unit cell of $a = 3.804(1)$ Å and $c = 11.993(2)$ Å.

Formation and superconductivity of 1212-type phase $\text{TlSr}_2(\text{Sr}_{0.5}\text{R}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ with $\text{R}=\text{Sc}$, Y and lanthanides

Y. Xin, Z.Z. Sheng, D.X. Gu and D.O. Pederson

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 31 January 1991

Revised manuscript received 2 April 1991

Nominal samples $\text{TlSr}_2(\text{Sr}_{0.5}\text{R}_{0.5})\text{Cu}_2\text{O}_x$ with $\text{R}=\text{Sc}$, Y and lanthanides, have been prepared, and investigated by X-ray diffraction analysis and resistance measurement. The sample with $\text{R}=\text{Y}$, Pr , Nd , Sm , Eu , Gd , Tb , Dy , Ho , Er , Tm , Yb , or Lu consists mainly of a tetragonal 1212-type phase $\text{TlSr}_2(\text{Sr}_{0.5}\text{R}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$, and exhibits a superconducting transition at about 90 K. The sample with $\text{R}=\text{Ce}$ forms a very pure 1212 phase, but is a semiconductor. The sample with $\text{R}=\text{Sc}$ forms essentially a 1201 phase, and is a semiconductor. The sample of $\text{R}=\text{La}$ consists of 1201 phase as its major phase and a 1212 phase as its minor phase, and shows two-step superconducting transitions at 40 K and 90 K. The results are discussed from the point of view of the average valence of Cu and the ionic size of the rare earth.

1. Introduction

The Tl-based 1212-type superconducting compound $(\text{Tl}, \text{M})\text{A}_2(\text{A}', \text{M}')\text{Cu}_2\text{O}_{7-\delta}$ was first identified in the TlBiSrCaCuO system by Haldar et al. [1], and in the TlBaCaCuO system by Parkin et al. [2]. The 1212-type phase has the following features:

- (1) its crystal structure is similar to that of the well-known 123 phase $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$;
- (2) it can be widely subjected to elemental substitutions, for example, M can be Pb or/and Bi, A can be Ba or/and Sr, A' can be Sr or/and Ca, and M' can be Ca or/and R ($\text{R}=\text{rare earths}$);
- (3) the T_c 's of this family vary from 70 K to 106 K and strongly depend on the species of the substitutes M and M' [1-17]. The $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_{7-\delta}$, an offspring of the 1212-type family, has T_c of 80-90 K [11,12]. Partial substitution of Pb for Tl in this compound has led to the first Ca-free $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_{7-\delta}$ with T_c above 100 K [16,17]. The rare earths play a very important role either in $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_{7-\delta}$ or $(\text{Tl}, \text{Pb})\text{Sr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_{7-\delta}$. However, the existing data are limited to $\text{R}=\text{Pr}$, Nd , Tb , and Er [11,12,16,17]. For a systematic knowledge of the effects of rare earths on the formation and superconductivity of the 1212 phase, we have carried

out experiments on all rare earths including Sc and Y. In this paper, we report the preparation of samples with starting composition of $\text{TlSr}_2(\text{Sr}_{0.5}\text{R}_{0.5})\text{Cu}_2\text{O}_x$ ($\text{R}=\text{Sc}$, Y , and lanthanides) and the results of characterization by powder X-ray diffraction and by resistance measurement. We choose the starting composition of $\text{TlSr}_2(\text{Sr}_{0.5}\text{R}_{0.5})\text{Cu}_2\text{O}_x$ because our previous experiments have showed that the sample of $\text{R}=\text{Pr}$ or Er with this starting composition forms nearly pure 1212 phase and exhibit good superconducting properties [18]. We will discuss the effects of different rare earths on the formation and superconductivity of the 1212 phase from the point of view of the ionic radius of R and the average valence of Cu.

2. Experimental

Samples for the present investigation were prepared using high purity (99.9% or higher) Tl_2O_3 , SrO , CuO , and rare earth oxides (R_2O_3 , except CeO_2 , Pr_6O_{11} , and Tb_4O_7). The preparation procedure, X-ray diffraction analysis, and resistance measurement are similar to those in refs. [16-18].

DERIVATIVES OF $TlSr_2CaCu_2O_7$ FROM ELEMENTAL SUBSTITUTIONS OF Pb FOR Tl, La FOR Sr, AND Y FOR Ca

Z. Z. Sheng, Y. F. Li, and D. O. Pederson

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

(Received 9 September 1991 by A. A. Maradudin)

$Tl(Sr,La)_2CaCu_2O_7$, $Tl(Sr,La)_2(Ca,Y)Cu_2O_7$, and $(Tl,Pb)(Sr,La)_2(Ca,Y)Cu_2O_7$ were synthesized and characterized. Thus, all derivatives of the 1212-type phase $TlSr_2CaCu_2O_7$ from elemental substitutions, Pb for Tl, La for Sr, or/and Y for Ca, have been synthesized. La and Y play a similar role in the substitutions. Pb is necessary to increase the T_c from 90 K to above 100 K in the double substitutions while it plays a role similar to La and Y in the single substitution. The triple substitution of Pb, La, and Y does not increase T_c to even higher. The optimal average Cu valence is 2.20 ± 0.05 , the same for all derivatives.

The Tl-based 1212-type phase $TlSr_2CaCu_2O_7$ itself can not be synthesized easily in the pure form and shows T_c from 0 to 80 K¹⁻³. However, if a metallic ion is substituted partially by a higher valence ion, for example, Ca^{2+} by R^{3+} (R = rare earths), the 1212 phase is stabilized and its superconducting behavior is improved^{4,7}. When the substitutes are Pb^{4+} (for Tl^{3+}), La^{3+} (for Sr^{2+}), and Y^{3+} (for Ca^{2+}), there are three single-substitution derivatives $(Tl,Pb)Sr_2CaCu_2O_7$, $Tl(Sr,La)_2CaCu_2O_7$, and $TlSr_2(Ca,Y)Cu_2O_7$, three double-substitution derivatives $(Tl,Pb)(Sr,La)_2CaCu_2O_7$, $(Tl,Pb)Sr_2(Ca,Y)Cu_2O_7$, and $Tl(Sr,La)_2(Ca,Y)Cu_2O_7$, and one triple-substitution derivative $(Tl,Pb)(Sr,La)_2(Ca,Y)Cu_2O_7$. To our knowledge, all the derivatives but $Tl(Sr,La)_2CaCu_2O_7$, $Tl(Sr,La)_2(Ca,Y)Cu_2O_7$, and $(Tl,Pb)(Sr,La)_2(Ca,Y)Cu_2O_7$ have been synthesized³⁻¹⁰. Therefore, the syntheses of the remaining three derivatives are of importance in the study of the effects of elemental substitutions on stability and superconductivity of the 1212 phase. In particular, the existing data showed that single substitution (Pb or Y) only reaches T_c of 80-90 K^{2,8}, and double substitutions (Pb and La, or Pb and Y) is necessary to enhance the T_c of the 1212 phase to above 100 K^{2,10}. Therefore, the syntheses of the remaining derivatives will clarify if the double substitution of La and Y also increases T_c to above 100 K, and if the triple substitution of Pb, La, and Y can reach T_c even higher than that of Pb double substitutions. In this paper, we report that we have synthesized and characterized the remaining three derivatives $Tl(Sr,La)_2CaCu_2O_7$, $Tl(Sr,La)_2(Ca,Y)Cu_2O_7$, and $(Tl,Pb)(Sr,La)_2(Ca,Y)Cu_2O_7$, and thus completed the syntheses of all derivatives of $TlSr_2CaCu_2O_7$ from elemental substitutions, Pb for Tl, La for Sr, or/and Y for Ca. The results are presented, and are discussed in the framework of average Cu valence by combining the published data.

Samples were prepared using high-purity Tl_2O_3 , PbO_2 , SrO , La_2O_3 , CaO , Y_2O_3 , and CuO . Appropriate amounts of component oxides were completely mixed and ground, and pressed into pellets with a diameter of 7 mm and a thickness of about 2-3 mm. The pellets were placed in a covered alumina crucible. The crucible with the contents was introduced into a preheated tube furnace, and heated at 1000 °C in flowing oxygen for 15 minutes, followed by furnace-cool to below 200 °C. The resulted samples were examined by powder x-ray diffraction analyses and resistance measurements. Powder x-ray diffraction analyses were carried out with $Cu-K\alpha$ radiation with the use of a DIANO DTM 1057 diffractometer. Resistance (ac, 27 Hz) was measured by the standard four-probe technique with silver paste contacts in a commercial APD closed-cycle refrigerator system with computer control and logging.

Three series of samples with nominal compositions of $Tl(Sr_{1-y}La_y)CaCu_2O_7$ with $y = 0.2, 0.3, 0.4, 0.5, 0.6,$ and 0.7 , $Tl(Sr_{2-y}La_y)(Ca_{0.8}Y_{0.2})Cu_2O_7$ with $y = 0.1, 0.2, 0.3, 0.4, 0.5,$ and 0.6 , and $(Tl_{1-x}Pb_x)(Sr_{1.8}La_{0.2})(Ca_{0.8}Y_{0.2})Cu_2O_7$ with $x = 0.0, 0.1, 0.2, 0.3,$ and 0.45 were prepared. Powder x-ray diffraction analyses showed

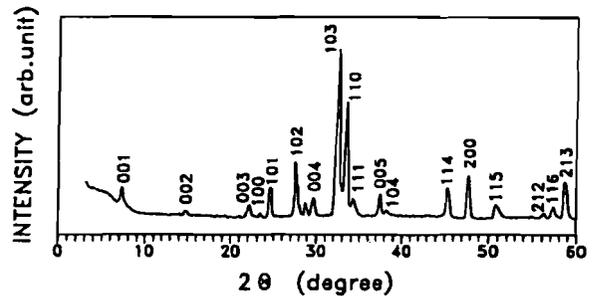


Figure 1 X-ray diffraction pattern for the sample $Tl(Sr_{1.8}La_{0.2})(Ca_{0.8}Y_{0.2})Cu_2O_7$, of $y = 0.4$.

that all the samples are nearly pure 1212 phase. The diffraction patterns can be well indexed based on a tetragonal unit cell with $a = 3.80 \text{ \AA}$ and $c = 12.0 \text{ \AA}$ (space group $P4/mmm$). As an example, Figure 1 shows the indexed x-ray diffraction pattern for the sample $Tl(Sr_{1.8}La_{0.2})(Ca_{0.8}Y_{0.2})Cu_2O_7$, of $y = 0.4$. The lattice parameters a and c for the samples are listed in Table I.

Table I Lattice parameters and T_c 's for $(Tl_{1-x}Pb_x)(Sr_{1.8}La_{0.2})(Ca_{1-2}Y_2)Cu_2O_7$

x	y	z	a(Å)	c(Å)	T_c (K) onset	T_c (K) zero-R
0.0	0.2	0.0	3.780	12.096	40	20
0.0	0.3	0.0	3.802	12.092	50	29
0.0	0.4	0.0	3.804	12.076	88	56
0.0	0.5	0.0	3.812	12.076	90	72
0.0	0.6	0.0	3.815	12.073	92	77
0.0	0.7	0.0	3.814	12.019	77	71
0.0	0.1	0.2	3.794	12.036	77	45
0.0	0.2	0.2	3.794	12.039	77	45
0.0	0.3	0.2	3.802	12.037	82	67
0.0	0.4	0.2	3.802	12.033	87	77
0.0	0.5	0.2	3.802	11.994	90	77
0.0	0.6	0.2	3.815	12.000	85	45
0.0	0.2	0.2	3.796	11.984	85	77
0.1	0.2	0.2	3.801	12.009	95	60
0.2	0.2	0.2	3.802	12.016	98	77
0.3	0.2	0.2	3.805	12.018	100	77
.45	0.2	0.2	3.808	12.025	102	60

Thermopower and Resistivity of 1212-Type Phase $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_{7-\delta}$

Y. XIN, Y. F. LI, D. FORD,
D. O. PEDERSON and Z. Z. SHENG

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

(Received July 3, 1991; accepted for publication July 20, 1991)

Nominal $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_x$ samples were prepared, and were investigated by powder X-ray diffraction analyses, and by resistivity and thermoelectric-power measurements. The samples with $y=0.0-0.5$ are nearly pure 1212-type phase $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_{7-\delta}$. The 1212 phase converts from semiconducting to superconducting at $y=0.1-0.2$, and exhibits the optimal superconducting behavior when $y=0.4-0.5$. In the range of 150-300 K, the thermopower values of the 1212 phase are nearly temperature-independent. The hole concentration calculated from the thermopower data using the Hubbard model in high temperature limit with strong on-site Coulomb interaction is quantitatively consistent with the $y/2$ value.

KEYWORDS: high T_c superconductor, $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_{7-\delta}$, thermopower, resistivity, Hubbard model, mixed Cu valence

The 1212-type phase $\text{MA}_2\text{A}'\text{Cu}_2\text{O}_{7-\delta}$, where M, A, and A' are metallic elements, is an analogue and a more general form of the 123 phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (the 123 phase can be written as $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$). While a large volume of data have been published for the 123 phase, the systematic data for the transport behavior of the 1212 phase are not available. In previous papers, we reported the formation and superconductivity of the Tl-based 1212 phase $\text{TlSr}_2(\text{R}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_{7-\delta}$ with $\text{R}=\text{Pr}$ and Er^{11} and $\text{TlSr}_2(\text{R}_{0.5}\text{Sr}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ with $\text{R}=\text{all rare earths}$.²⁾ In this paper we further present the detailed data from resistivity and thermoelectric-power measurements for $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_{7-\delta}$. The thermoelectric power data are particularly interesting in that they can be quantitatively explained in terms of the Hubbard model in high temperature limit with strong on-site Coulomb interaction.

Nominal $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_x$ samples with $y=0.0-1.0$ were synthesized using the solid reaction. Appropriate amounts of high purity Tl_2O_3 , SrO , Er_2O_3 , and CuO were mixed, ground, and then pelletized. The pellets were put in an alumina crucible with a cover, and were heated in a preheated furnace at about 1000°C in flowing oxygen for 30 minutes. After heating, the pellets were furnace-cooled to below 200°C . Resistivity of the samples was measured by the four-probe technique with an ac frequency of 27 Hz. Thermoelectric power was measured using a modified dc differential method.³⁾ Powder X-ray diffraction measurement was performed by $\text{Cu-K}\alpha$ radiation using a DIANO DTM 1057 diffractometer.

Powder X-ray diffraction analyses show that the $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_x$ samples with $y=0.0-0.5$ are almost pure 1212-type phase, whereas the samples with $y>0.5$ contain a 1201-type phase besides the 1212 phase. The content of the 1201 phase increases with y , and the sample of $y=1.0$ consists essentially of the 1201 phase. The 1212 phase has a tetragonal unit cell (space group $\text{P4}/\text{mmm}$) with lattice parameters of $a \sim$

3.81 \AA and $c \sim 12.00 \text{ \AA}$. This structure corresponds to $\text{TlSr}_2(\text{Sr}, \text{R})\text{Cu}_2\text{O}_{7-\delta}$. Figure 1 shows the schematic drawing of the 1212 phase. The 1201 phase also has a tetragonal unit cell (space group $\text{P4}/\text{mmm}$) with $a \sim 3.75 \text{ \AA}$ and $c \sim 8.90 \text{ \AA}$. Figure 2 shows the diffraction patterns for the samples with $y=0.0, 0.3$, and 0.7 . Table I lists the unit cell parameters and the volume fraction of the 1212 phase for the samples of $y=0.0-0.7$. The volume fraction was estimated based on the comparison of intensity of the (103) reflection in the 1212 phase with intensity of the (102) one in the 1201 phase.

The resistivity(ρ)-temperature(T) plots for the $\text{TlSr}_2(\text{Er}_{1-y}\text{Sr}_y)\text{Cu}_2\text{O}_x$ samples are shown in Figs. 3(a) and 3(b). The samples with $y=0.0$ and 0.1 exhibit a semiconducting behavior. The sample with $y=0.2$ shows no significant change in resistivity from 300 to 150 K. The ρ - T curve starts to go up at about 150 K until the tem-

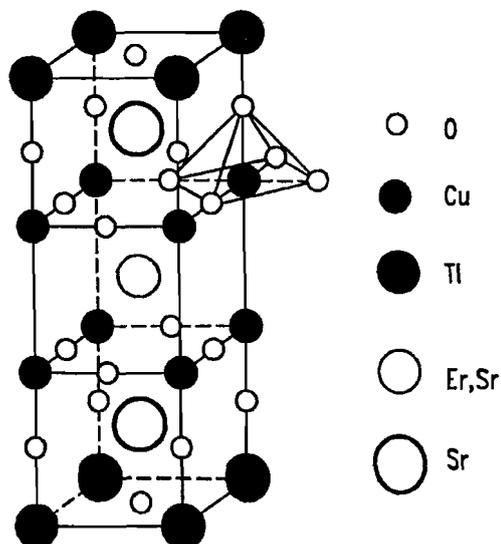


Fig. 1. Schematic structure of the 1212 phase $\text{TlSr}_2(\text{Er}, \text{Sr})\text{Cu}_2\text{O}_{7-\delta}$.

Study on Zn-, Cd-, or Hg-addition into TlBaCuO

Y. Xin and Z. Z. Sheng

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

(Received 1 May 1990; accepted for publication 2 August 1990)

Nominal ZnTlBaCuO_{4.5}, CdTlBaCuO_{4.5}, and HgTlBaCuO_{4.5} samples have been prepared under different conditions and have been studied by resistance and ac-susceptibility measurements compared to nominal TlBaCuO_{3.5} samples. In general, the ZnTlBaCuO_{4.5} samples required less strict heating conditions to reach zero resistance near liquid nitrogen temperature; the CdTlBaCuO_{4.5} samples had lower T_c ; the HgTlBaCuO_{4.5} samples showed slightly improved T_c at certain conditions. In contrast to La_{2-x}Sr_xCuO₄, Zn-addition did not significantly depress T_c of TlBaCuO. This observation is worthy to be investigated further. Hardness of the ZnTlBaCuO_{4.5} and CdTlBaCuO_{4.5} samples was greatly increased, which could have importance in the practical applications of these materials.

INTRODUCTION

The discovery of the 90 K TlBaCuO system^{1,2} and the 120-K TlBaCaCuO system^{3,4} has stimulated worldwide experimental investigations on Tl-based superconductors. A series of superconducting compounds with a general formula of Tl_mBa₂Ca_{n-1}Cu_nO_{1.5m+2n+1}, with $m = 1-2$ and $n = 1-5$, have been rapidly identified.⁵⁻⁹ Among them, Tl₂Ba₂Ca₂Cu₃O₁₀ (2223 phase) and Tl₂Ba₂CuO₆ (2201 phase) are particularly interesting. The former holds the record of the highest reproducible T_c of 125 K,^{4,6,7} whereas the latter has superconducting behavior strongly dependent on preparation conditions and has T_c from 0 K to above 90 K.^{1,2,7,8,10-14}

Historically, the 120-K TlBaCaCuO system was discovered by adding Ca into the 90-K TlBaCuO parent system.³ In view of this fact and in view of the interesting behaviors of Tl₂Ba₂CuO₆, we have carried out extensive elemental addition experiments for the TlBaCuO system. We have reported the results of addition of 4+ valence element Ce, Ti, Zr, or Hf.^{15,16} In this paper, we report the results of addition of 2+ valence element Zn, Cd, or Hg. The results showed that in general, Zn changed T_c slightly, Cd depressed T_c , and Hg could increase T_c slightly if a proper preparation condition was used.

EXPERIMENT

The samples were made using a two-step procedure with high purity Tl₂O₃, BaO₂, CuO, and ZnO, CdO, or HgO. The first step was the making of a BaCuO precursor. According to our experience and the literature,¹⁷ excessive Cu in TlBaCuO is helpful to reach higher T_c . For this reason and for exploring possible new superconducting phases, we made BaCuO₂ precursor rather than Ba₂CuO₃. Appropriate amounts of BaO₂ and CuO were mixed and ground in an agate mortar. The resulting mixture was put into a tube furnace, and was heated at 900 °C in air for 20 h. The heated mixture was taken out of the furnace and ground again. The second step was the making of samples with nominal compositions of ZnTlBaCuO_{4.5}, CdTlBaCuO_{4.5}, and HgTlBaCuO_{4.5}. For comparison, samples with nominal composition of TlBaCuO_{3.5} were also

made. Appropriate amounts of BaCuO₂, Tl₂O₃, and ZnO, CdO, or HgO were mixed and ground completely in an agate mortar. The resulting powders were pressed into pellets of about 12 mm in diameter and 1-2 mm in thickness using a hydraulic press. The applied pressure was about 7000 kg/cm². All samples were sintered in a tube furnace with a quartz tube. The atmosphere was created by flowing a gas through the tube. The furnace was preheated to a certain temperature. The samples were put on a piece of gold foil in an alumina boat. The boat and contents were quickly introduced into the preheated furnace and heated for a certain period of time. The samples were then quenched to room temperature by removing the boat from the furnace. Five batches of samples were prepared. Preparation conditions for each batch are summarized in Table I. For simplicity, nominal samples TlBaCuO_{3.5}, ZnTlBaCuO_{4.5}, CdTlBaCuO_{4.5}, and HgTlBaCuO_{4.5} are denoted by Tl, Zn, Cd, and Hg, respectively. The number followed Tl, Zn, Cd, and Hg are batch No. Therefore, Zn-1 represents the sample ZnTlBaCuO_{4.5} made in batch No. 1, and so on.

Resistance was measured by a four-probe technique with an ac of 27 Hz. The sample and the leads were connected with silver paste. The ac susceptibility was measured using the standard mutual inductance technique similar to that by Norton¹⁸ with an ac of 500 Hz. Both resistance and ac susceptibility measurements were carried

TABLE I. Summary of preparation conditions for nominal samples TlBaCuO_{3.5}, ZnTlBaCuO_{4.5}, CdTlBaCuO_{4.5}, and HgTlBaCuO_{4.5}.

Batch No.	Heat time (min)	Temperature (°C)	Atmosphere
1	5	900-905	argon
2	5	900-905	oxygen
3	6	910-915	oxygen
4 ^a	8	915-923	air
5 ^b	6	920-925	flowing oxygen 2 min and then cutoff

^aHgTlBaCuO_{4.5} sample melted partly.

^bAll samples melted partly.

Superconductivity above 100 K in the Ca-free Tl-Pb-Sr-Pr-Cu-O system

Z.Z. Sheng, Y. Xin, J.M. Meason and L.A. Burchfield

Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA

Received 11 March 1990

Revised manuscript received 24 July 1990

Superconductivity up to 105 K was observed in the Ca-free Tl-Pb-Sr-Pr-Cu-O system. Powder X-ray diffraction analyses showed that a 132 phase was responsible for the observed superconductivity. $(\text{Tl}_{0.8}\text{Pb}_{0.2})(\text{Sr}_{2.5}\text{Pr}_{0.5})\text{Cu}_2\text{O}_x$ was nearly single 132 phase, and had a tetragonal unit cell with $a = 3.84091(38) \text{ \AA}$ and $c = 12.1952(12) \text{ \AA}$.

The discovery of the 110 K Bi-Sr-Ca-Cu-O system [1] and the 120 K Tl-Ba-Ca-Cu-O system [2] has led to a number of new superconducting systems above 100 K. Among them are Tl-Pb-Sr-Ca-Cu-O [3] and Tl-Bi-Sr-Ca-Cu-O system [4]. Although 100 K superconductivity in the Ca-free Tl-Bi-Ba-Sr-Cu-O system and Tl-Ba-Zr-Cu-O system has been reported [4,5], the systems showing reproducible superconductivity above 100 K all contain Ca. The Ca-free Tl-Sr-RE-Cu-O system (RE=rare earths) was found to be superconducting at about 40 K [6] and 90 K [7]. The phases responsible for the 40 K and 90 K superconductivity were identified to be $\text{Tl}(\text{Sr}_{2-y}\text{RE}_y)\text{CuO}_z$ (121 phase) and $\text{Tl}(\text{Sr}_{3-y}\text{RE}_y)\text{Cu}_2\text{O}_z$ (132 phase) [7]. Further work showed that when Tl was partially substituted by Pb, the Tl-Pb-Sr-RE-Cu-O system could form a superconducting phase with onset temperatures up to 105 K. The phase was identified to be $(\text{Tl}_{1-x}\text{Pb}_x)(\text{Sr}_{3-y}\text{RE}_y)\text{Cu}_2\text{O}_z$ (132 phase). To our knowledge, this is the first observation of reproducible superconductivity above 100 K in a Ca-free system. In this paper, we present the results using Pr as an example of rare earths. The results with other rare earths will be published in a separate paper.

Samples were prepared using high-purity Tl_2O_3 , PbO_2 (or $\text{Pb}(\text{NO}_3)_2$), SrO (or SrCO_3 and $\text{Sr}(\text{NO}_3)_2$), Pr_6O_{11} and CuO . Two typical preparation procedures were employed. In procedure I,

component compounds with a certain metallic atom ratio were completely mixed, ground and pressed into a pellet with a diameter of 7 or 15 mm and a thickness of 1-2 mm. The pellet was heated at about 720°C for 5-20 h in air. The pellet was then heated in a tube furnace at $980-1000^\circ\text{C}$ in flowing oxygen for about 10 min, followed by quenching or furnace cooling. In procedure II, component oxides with a certain metallic atom ratio were mixed, ground, and pressed into a pellet with a diameter of 15 mm and a thickness of about 2 mm. The pellet was heated in a tube furnace at about 1000°C in flowing oxygen for 30 min, followed by furnace cooling. The samples were examined by resistance, AC susceptibility and thermoelectric power measurements, and by powder X-ray diffraction analyses. Resistance (AC, 27 Hz) was measured by the standard four-probe technique with silver paste contacts. AC (500 Hz) susceptibility was measured using the standard mutual inductance method. Thermoelectric power was measured using a set of apparatus described in ref. [8]. All measurements were made with computer control and processing, and were called out in a commercial APD refrigerator. Powder X-ray diffraction was carried out with $\text{Cu-K}\alpha$ radiation with use of a DIANO DIM 1057 diffractometer.

Figure 1 shows resistance-temperature dependences for a Pb-free Tl-Sr-Pr-Cu-O sample (A) and a nominal $(\text{Tl}_{0.8}\text{Pb}_{0.2})(\text{Sr}_2\text{Pr})\text{Cu}_2\text{O}_x$ sample (B)

VANADIUM-LEAD SUBSTITUTED 2223 Bi-Sr-Ca-Cu-O SUPERCONDUCTORS

Ying Xin, Z. Z. Sheng and F. T. Chan

Physics Department, University of Arkansas, AR, USA

and

P. C. W. Fung and K. W. Wong*

Physics Department, University of Hong Kong, Hong Kong

(Received 20 August 1990 by W. Y. Kuan)

Following up our previous work [24] on the fabrication of the $\text{Bi}_{2-x}\text{V}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $\text{Bi}_{2-x}\text{V}_x\text{Sr}_2\text{CaCu}_3\text{O}_8$ superconductors with x ranging from a fraction to unity we report here the fabrication of double-substituted superconducting ceramics satisfying the nominal stoichiometric ratio of $\text{Bi}_{2-(x+y)}\text{V}_x\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$, where x, y run from small fractions to 0.7. For most of the samples, the lower $T_c = 80\text{ K}$ phase disappears, leaving the higher $T_c = 110\text{ K}$ phase. Since a wide range of combinations of x, y can lead to similar superconductors and that the pure $T_c = 110\text{ K}$ phase samples are associated with larger values of $(x + y)$, we believe that the V-Pb substitution is significantly different from the Pb-doped or Pb-Sb-doped cases in the basic crystal structure. Our samples are found to pass through the paramagnetic to the diamagnetic state as the temperature is decreased across the critical temperature region.

1. INTRODUCTION

IT HAS been found that there are quite a large number of crystal structures or phases that can co-exist or exist under separate conditions in the class of Bi-Sr-Ca-Cu-O superconductors [1-5]. For examples, there are nominal compositions satisfying Bi: Sr: Ca: Cu = 2:2:0:1 ($T_c \sim 10\text{ K}$), 1:1:1:2 ($T_c < 80\text{ K}$), 2:2:1:2 ($T_c \sim 80\text{ K}$) and 2:2:2:3 ($T_c \sim 110\text{ K}$). While the lowest order phase (2201) is mono-clinic, the other phases so far reported seem to have average orthorhombic structures with different crystal parameters. The (2201), (2212) and (2223) phases have single, double, and triple layers of CuO_2 plane in the sub-unit cell respectively, and more CuO_2 planes are believed to be associated with higher values of T_c . It is therefore important to enhance the (2223) 110 K phase by using various methods of preparation [e.g. 6, 7] or by doping. In fact, Al, La, Sb and Pb doped in the Bi-type superconductors [8-21] have been reported and the last member Pb has been found to be a rather good dopant in enhancing the 110 K phase. The double doping with Pb-Sb has aroused interest along this line [22, 23]. However, only a very limited amount of the

dopant can replace Bi, in the nominal composition ($< 40\%$).

In order to understand more fully about the role played by dopants of the high T_c phases of the Bi-type superconductors, it is crucial to find out whether other dopant(s), apart from Pb, could also enhance the formation of the high T_c phase(s). Even more important it is crucial to find out whether any other element can have an equal standing as Bi; at the end, we hope that Bi can be replaced completely such that a new superconductor class can be found. The recent band structure calculations [24] on a hypothetical structure same as the bismuth structure but with the composition $\text{V}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ produce a band structure favouring the formation of condensed charged excitons. According to the EEM theory [25, 26] a superconductor would result if such a condition is satisfied. Thus such an estimation suggests that vanadium might be used to replace Bi, at least partially. With this motivation in mind, we have attempted and have succeeded in replacing Bi by V in the predetermined (2212) and (2223) superconductors up to at least a ration of $r = \text{V/Bi} = 1$. We have demonstrated that the $R-T$ curves show clear sudden drops at about 110 K, though the $T_c (R = 0)$ value is only several degrees above that of the pure Bi-type superconductor prepared under same conditions. The readiness in the formation of the

* Permanent address: Physics Department, University of Kansas, KS 66045, USA.

DOUBLE TRANSITION IN CALCIUM-123 ($\text{CaSr}_2\text{Cu}_3\text{O}_y$) SUPERCONDUCTOR

Xin Fei, D.F. Lu, G.F. Sun and K.W. Wong

Physics Department, University of Kansas, KS 66045, USA

F.T. Chan, Z.Z. Sheng and Ying Xin

Physics Department, University of Arkansas, AR, USA

P.C.W. Fung and C.C. Lam*

Physics Department, University of Hong Kong, Hong Kong

and

W.Y. Ching and Y. Xu

University of Missouri, Kansas City, MO, USA

(Received 20 August 1990 by W.Y. Kuan)

The Ca^{2+} is successfully substituted for the 3+ rare earth element in the 123 ceramic structure. A double phase transition is observed in oxygen deficient samples. A superconducting transition onset occurs at 90 K, and all resistivity vanishes at 73 K. However, at a lower temperature of 50 K the sample exhibits a superconducting to insulating transition. The double transition in $R-T$ is accompanied by a corresponding double magnetic transition in $\chi-T$.

1. INTRODUCTION

THE Y-123 superconducting ceramic appears to be the only cuprate so far found that is stoichiometric [1], which makes the study of its electronic structure [2-5] less complicated. However, it is also well known that oxygen deficiency can occur in this material, and as oxygen molar ratio in the compound reduces below 6.5, the compound goes through an antiferromagnetic phase transition at a temperature close to the original non oxygen deficient superconducting critical temperature, and no superconducting phase is realized in this sample. This apparent antiferromagnetic phase transition near the superconducting critical temperature under oxygen deficient condition has drawn theorists to speculate that there is a coupling between the spin-spin interaction and the superconducting mechanism [6]. Since most high temperature superconductors contain copper, which has a d -orbital electron, it is difficult to delineate the magnetic moment interaction from charge electronic interactions which is responsible for the BCS [7] low T_c superconducting mechanism. We have proposed a purely charge

electronic model [8] which has ignored the magnetic moment interacting terms for the explanation of the high T_c mechanism. This theory has been received with skepticism by others and is rightly so because of the above mentioned presence of an antiferromagnetic phase in some of the ceramic cuprate superconductors. Another rather puzzling fact also dealing with the Y-123 compound, is that there exists a tetragonal phase with 6 oxygen in the unit cell. This phase has similar lattice parameters and rather close electronic structures. Except that the copper oxide chain is replaced by a pure copper plane, thus in the electronic structure intrinsic hole states due to the copper oxide chain is missing [9]. The tetragonal Y-123 phase is not a superconductor. In the earlier days, people speculated the importance of the copper oxygen chain structure. Unfortunately, other experimental investigations, such as μ -spin relaxation, internal friction experiments [10] etc., all points to the contribution of the copper oxygen plane instead. Thus it appears to us that the oxygen deficiency in the copper oxygen chain serves more in enhancing the formation of the antiferromagnetic phase rather than the superconducting phase. In fact, since the presence of the antiferromagnetic phase in the oxygen deficient compound also precludes the existence of superconductivity in these

* Permanent address: Department of Applied Science, City Polytechnic of Hong Kong.

THERMOELECTRIC POWER OF Tl-Ca-Ba-Cu-O AND Pr-Tl-Sr-Ca-Cu-O HIGH T_c SUPERCONDUCTORS

A.K. Bhatnagar^{*1}, R. Pan¹, D.G. Naugle¹, P.J. Squattrito² and A. Clearfield²

¹Physics Department; ²Chemistry Department, Texas A & M University, College Station, TX 77843 USA
and

Z.Z. Sheng, Q.A. Shams and A.M. Hermann

Department of Physics, University of Arkansas, Fayetteville, AR 72701 USA

(Received 28 July 1989 by M. Cardona)

The resistance and the thermoelectric power of thallium based high T_c 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_c , 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_c , is quite different than that observed for $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors.

INTRODUCTION

AFTER THE discovery [1] of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ high T_c superconductors with $T_c = 90$ K where R stands for a rare earth element, a higher T_c of about 100-125 K was obtained in Tl-Ca-Ba-Cu-O superconductors [2]. In particular, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ was found to have a T_c of 120-125 K. Recently, a new family of thallium oxide based superconductors, R-Tl-Sr-Ca-Cu-O, have been synthesized with T_c 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 T_c above 77 K.

The structure of thallium based oxide superconductors is tetragonal and consists of double, for $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_8$, or triple, for $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$, CuO_2 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 $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_8$ (referred to hereafter as the 2 1 2 2 phase), and only Ca substitution on the Tl sites

in $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (referred to hereafter as the 2 2 2 3 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 2 2 2 3 Tl compound was found ($x = 9.86$ instead of 10, where x is the number of oxygen atoms). Unlike $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors, there are no Cu-O chains in Tl-Ca-Ba-Cu-O superconductors. Thus, Cu-O planes seems to be the primary requirement for superconductivity in the cuprate superconductors. Further, unlike $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors, the oxygen content in Tl-Ca-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 Tl-Ca-Ba-Cu-O superconductors in comparison with those of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors.

Electronic transport properties of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$, in particular those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ 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 Tl-Ca-Ba-Cu-O superconductors. Besides the usual resistance measurements to determine the resistive

* Present address School of Physics, University of Hyderabad, Hyderabad 500 134, Andhra Pradesh, India.