

## Formation of Superconducting $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ from Coprecipitated Oxalates

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Received February 9, 1990

The conditions for the coprecipitation of  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cu}^{2+}$  as oxalates are reported. These oxalates were used as precursors for the formation of  $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  superconducting ceramics. The behavior of the oxalates upon heat treatment was studied by thermogravimetry. Both the oxalates and the superconducting oxides were analyzed and characterized by atomic absorption spectroscopy and by X-ray diffraction. For  $0.2 \leq y \leq 0.4$  and proper heat treatment of the oxalates, followed by compression of the oxides and by sintering, single-phase ceramic samples with a zero resistance temperature of  $T_c(0) \sim 106$  K can be produced in a convenient way. © 1990 Academic Press, Inc.

### 1. Introduction

For the new high-temperature superconductor (HTS) Bi–Sr–Ca–Cu–O transition temperatures ( $T_c$ ) of up to 110 K were reported (1, 2). Compounds of the type  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+\delta}$  ( $\delta$  being close to zero) show transition temperatures of 10, 85, and 110 K, depending on whether  $n$  is 1, 2, or 3 (3, 4). However, the pure high  $T_c$ -phase (110 K phase) observed for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  is difficult to obtain. Its synthesis requires very long calcination times at temperatures close to the solidus temperature of the system (5). Another way to obtain the high  $T_c$ -phase is based on the partial

substitution of  $\text{Bi}^{3+}$  by  $\text{Pb}^{2+}$  (6, 7). The precursors most commonly employed in the fabrication of both pure and Pb-doped Bi–Sr–Ca–Cu–O superconductors are  $\text{PbO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{SrCO}_3$ , and  $\text{CaCO}_3$  (1, 3, 4). Appropriate mixtures of these compounds are converted into the desired HTS phase by solid-state reactions. Until now there seem to have been very few investigations employing *wet* chemical techniques to fabricate precursor materials for Bi–Sr–Ca–Cu–O superconductors (6, 8, 9). To our knowledge, only the coprecipitation of oxalates was reported (8). This published coprecipitation method is based on the reaction of the respective cations with oxalic acid in dilute aqueous nitric acid, followed by a neutralization step with  $\text{NaOH}$ . This

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procedure led to amorphous precursor material. Difficulties were encountered by the formation of basic bismuth salts, by the comparably high solubility of strontium oxalate in this medium, and by the complex formation of strontium oxalate in excess oxalic acid. The ceramics fabricated from these precursors were all multiphase including phases described as  $\text{BiSrCaCu}_2\text{O}_{6-z}$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+z}$ .

In this paper we shall report on the coprecipitation of precursor material in the form of oxalates. These oxalates can be conveniently converted by proper heat treatment to almost pure single-phase ceramic samples of  $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  with a zero-resistance temperature of 106 K.

## 2. Experimental and Results

### 2.1. Apparatus

X-ray diffraction spectra were obtained in a Geigerflex D-max IIa (Rigaku, Japan) employing  $\text{CuK}\alpha$  radiation. Atomic absorption analysis (AAS) was performed on a UNICAM SP1900 atomic absorption spectrophotometer. Thermogravimetric studies were carried out on a TG-770 (Stanton Redcraft, UK). A Stereoscan 200 (Cambridge, UK) instrument was used for scanning electron microscopy. The change in the resistance with temperature was measured by the standard four-point probe DC technique.

### 2.2. Analysis

For the determination of the concentrations of  $\text{Bi}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cu}^{2+}$ , 0.1 g of the oxalates was dissolved in 200 ml of 10 vol% nitric acid. In case of the oxidic compounds samples of 0.03 g were dissolved in 1 ml conc. hydrochloric acid and diluted to 100 ml with 99 ml of 10 vol% nitric acid. For the determination of the  $\text{Pb}^{2+}$  concentration, 0.1 g of the oxalate or 0.05 g of the

oxidic samples, respectively, was dissolved in 1 ml of hydrochloric acid and diluted to 20 ml with 10 vol% nitric acid. The cations in solution were analyzed by AAS at the following wave lengths: Bi, 223.06 nm; Pb, 283.31 nm; Ca, 422.67 nm; Sr, 460.73 nm; Cu, 324.75 nm. The amount of  $\text{Cu}^{3+}$  was analyzed using the following modification of a published procedure (10): 0.2 g of the oxidic samples was added to a solution containing 0.02 mole  $\text{dm}^{-3}$   $\text{FeSO}_4$ , 1.5 mole  $\text{dm}^{-3}$  sulfuric, and 1.5 mole  $\text{dm}^{-3}$  hydrochloric acid. Upon dissolution of the compound the unreacted  $\text{Fe}^{2+}$  was titrated with a 0.02 mole  $\text{dm}^{-3}$   $\text{K}_2\text{Cr}_2\text{O}_7$  with diphenylamine as indicator (color change from green to violet). Prior to the end point 2 ml of conc. phosphoric acid was added as complexing agent.

The oxalate anion was determined by a standard permanganate titration. The water content of the individual oxalates was derived from thermogravimetric measurements.

### 2.3. The Precipitation of the Oxalates

The precursor compounds for the  $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  ( $y$ : 0 to 0.4) material were precipitated as oxalates in the following manner:  $\text{SrCO}_3$  (Merck, extra pure),  $\text{Bi}_2\text{O}_3$  (Merck, extra pure),  $\text{CaCO}_3$  (Merck, volumetric standard),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (Merck, >99%), and  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3 \text{H}_2\text{O}$  (Merck, >99.5%) were dissolved in such quantities in 25 vol% acetic acid that the solution contained 0.02 mole  $\text{dm}^{-3}$   $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  as well as 0.03 mole  $\text{dm}^{-3}$   $\text{Cu}^{2+}$ . Depending on the desired final composition of the superconducting material the concentration of  $\text{Bi}^{3+}$  varied between 0.016 and 0.02 mole  $\text{dm}^{-3}$  and the concentration of  $\text{Pb}^{2+}$  from 0.004 mole  $\text{dm}^{-3}$  to zero. Clear, blue solutions were obtained in all cases. In a typical experiment 65 ml of a 0.8 mole  $\text{dm}^{-3}$  aqueous solution of oxalic acid (Merck, >99.5%) was added dropwise under stirring into 500 ml of the solution con-

taining the cations. Following the addition of the oxalic acid, the mixture was stirred for another hour and kept overnight. Upon filtration the precipitate was washed twice with 50 ml of distilled water and then dried at  $80^\circ\text{C}$  for 20 hr. The filtrate was analyzed by atomic absorption spectroscopy (AAS). Although the results varied slightly from experiment to experiment, the AAS analysis showed that less than 0.2% of the original amount of  $\text{Bi}^{3+}$ , less than 0.5% of  $\text{Pb}^{2+}$ , less than 1.9% of  $\text{Sr}^{2+}$ , less than 1.5% of  $\text{Ca}^{2+}$ , and less than 1.0% of  $\text{Cu}^{2+}$  remained in solution.

This procedure was also employed to prepare the following individual oxalates:  $\text{Pb}(\text{C}_2\text{O}_4)$ ,  $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ ,  $\text{Sr}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ , and  $\text{Cu}(\text{C}_2\text{O}_4) \cdot 2.5 \text{H}_2\text{O}$ . The precipitation of  $\text{Bi}^{3+}$  as oxalate under the above conditions yielded a compound, which based on our analysis can best be described as  $\text{Bi}(\text{OH})_{0.5}(\text{C}_2\text{O}_4)_{1.25}$ .

In order to obtain a more detailed picture of the coprecipitation process, oxalic acid was added stepwise to a solution containing  $0.016 \text{ mole dm}^{-3} \text{ Bi}^{3+}$ ,  $0.004 \text{ mole dm}^{-3} \text{ Pb}^{2+}$ ,  $0.02 \text{ mole dm}^{-3} \text{ Sr}^{2+}$ ,  $0.02 \text{ mole dm}^{-3} \text{ Ca}^{2+}$ , and  $0.03 \text{ mole dm}^{-3} \text{ Cu}^{2+}$ . Following each step the respective concentrations of

the cations remaining in solution were analyzed by AAS. The results of this investigation are given in Fig. 1. In this figure the concentrations of each cation are given as ratio of the concentration found in the supernatants to the original concentration of the respective cation. The amount of oxalic acid is expressed by the ratio of the charge brought in by the  $(\text{C}_2\text{O}_4)^{2-}$  ions to the total charge of the metal ions in the original solution. Thus the ratio of one corresponds to the amount of oxalic acid necessary to precipitate all of the cations originally present in solution. The figure shows clearly that  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  precipitate before the  $\text{Bi}^{3+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$ .

To further study the precipitation behavior of the above composition, the solid precipitate obtained from a solution, when only one-seventh of the required stoichiometric amount of oxalic acid was added, was analyzed by X-ray diffraction. This precipitate showed essentially the same spectrum as that of pure  $\text{Cu}(\text{C}_2\text{O}_4) \cdot 2.5 \text{H}_2\text{O}$  (Fig. 2a). The cations, which remained in solution, were then also precipitated and the crystals again analyzed by X-ray diffraction. The spectrum obtained for these crystals did not show any features characteristic of the individual oxalates  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , or  $\text{Bi}^{3+}$  (Fig. 2b). Surprisingly, despite the quite different precipitation behavior of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on the one hand and of  $\text{Bi}^{3+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$  on the other, the X-ray pattern of the coprecipitated oxalate (Fig. 2c) did not show features common with those of the pattern obtained for  $\text{Cu}(\text{C}_2\text{O}_4) \cdot 2.5 \text{H}_2\text{O}$ , nor with those of any of the other individual oxalates of  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{Sr}^{2+}$ . From these investigations we conclude that the oxalate crystals employed as precursor material represent a proper coprecipitate.

All oxalate precipitates were crystalline and yielded sharp X-ray diffraction patterns. The particle size of the coprecipitated oxalates, as measured by optical and

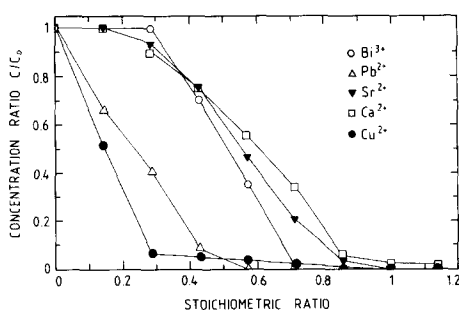


FIG. 1. Concentration of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  in solution relative to the respective concentration in the starting solution as a function of the amount of oxalic acid added. Original concentrations in solution:  $\text{Bi}^{3+}$ ,  $0.016 \text{ mole dm}^{-3}$ ;  $\text{Pb}^{2+}$ ,  $0.004 \text{ mole dm}^{-3}$ ;  $\text{Sr}^{2+}$ ,  $0.02 \text{ mole dm}^{-3}$ ;  $\text{Ca}^{2+}$ ,  $0.02 \text{ mole dm}^{-3}$ ;  $\text{Cu}^{2+}$ ,  $0.03 \text{ mole dm}^{-3}$ .

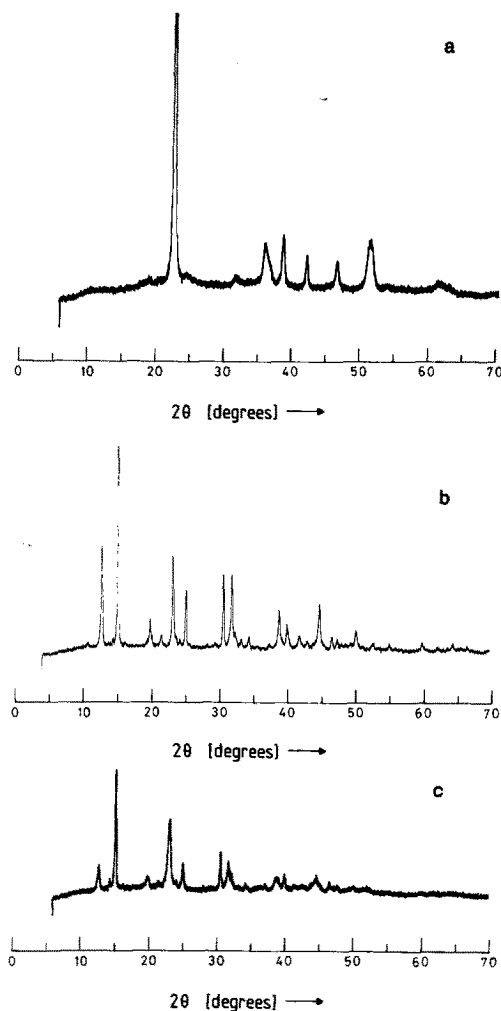


FIG. 2. X-ray diffraction patterns of some of the oxalates synthesized. (a)  $\text{Cu}(\text{C}_2\text{O}_4) \cdot 2.5 \text{H}_2\text{O}$ ; (b)  $\text{Bi}^{3+}$ -,  $\text{Sr}^{2+}$ -, and  $\text{Ca}^{2+}$ -coprecipitated oxalate; (c)  $\text{Bi}^{3+}$ -,  $\text{Pb}^{2+}$ -,  $\text{Sr}^{2+}$ -,  $\text{Ca}^{2+}$ -, and  $\text{Cu}^{2+}$ -coprecipitated oxalate.

scanning electron microscopy, was found to be below  $1 \mu\text{m}$ .

#### 2.4. Thermogravimetry

The thermogravimetric measurements on coprecipitated and individual oxalates were performed under argon atmosphere and at a heating rate of  $5 \text{ K min}^{-1}$ . The weight changes as a function of the temperature of

the coprecipitated oxalates were compared with the thermogravimetric behavior of the individual oxalates. Such comparisons permit the interpretation of the heating curve obtained for the coprecipitated oxalates as given in Fig. 3. The weight changes observed up to temperatures of about  $200^\circ\text{C}$  originate from the loss of water. The rather dramatic weight loss at around  $300^\circ\text{C}$  is caused by the conversion of the copper and bismuth oxalate to the oxides, followed by the conversion of calcium and strontium oxalate to the respective carbonates. The thermogravimetric behavior up to  $600^\circ\text{C}$  is similar to that observed for the individual oxalates. For temperatures above  $600^\circ\text{C}$ , however, significant differences in the behavior of the coprecipitated oxalates and the individual oxalates, measured under the same conditions, are revealed. The weight loss observed in the temperature range between  $600$  and  $900^\circ\text{C}$  is due to the loss of  $\text{CO}_2$  from  $\text{CaCO}_3$  and  $\text{SrCO}_3$ . These decomposition reactions occur at considerably lower temperatures than those measured on pure calcium and pure strontium oxalates, where these transformations have been observed in different temperature regimes namely between  $700$  and  $900^\circ\text{C}$  for  $\text{CaCO}_3$  and between  $900$  and  $1100^\circ\text{C}$  for  $\text{SrCO}_3$ .

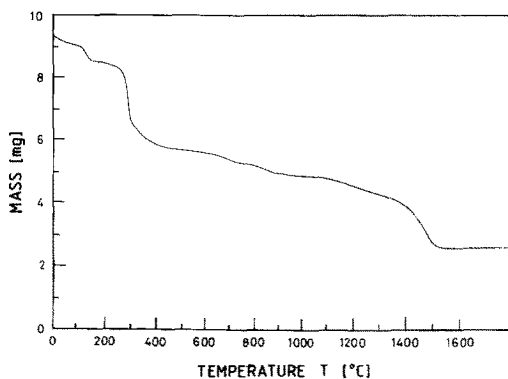


FIG. 3. Thermogravimetry curve of coprecipitated  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  oxalate.

TABLE I

CONCENTRATION OF THE CATIONS IN THE COPRECIPITATED OXALATES AND THE CALCINED Bi-Pb-Sr-Ca-Cu OXIDES AS WELL AS THE MOLAR RATIOS OF THE CATIONS AND THE CONDITIONS FOR CALCINATION

| Compound              | Concentration in wt%<br>(Molar ratios of cations) <sup>a</sup> |                |                |                 |              | Calcination conditions |           |
|-----------------------|----------------------------------------------------------------|----------------|----------------|-----------------|--------------|------------------------|-----------|
|                       |                                                                |                |                |                 |              | Temp (°C)              | Time (hr) |
| Solution <sup>b</sup> | (1.8)                                                          | (0.2)          | (2)            | (2)             | (3)          |                        |           |
| Oxalate               | 18.33<br>(1.64)                                                | 1.97<br>(0.18) | 4.16<br>(1.94) | 9.00<br>(1.92)  | 10.20<br>(3) |                        |           |
| Oxide                 | 36.30<br>(1.77)                                                | 2.54<br>(0.17) | 8.13<br>(2.05) | 16.93<br>(1.95) | 18.83<br>(3) | 850                    | 160       |
| Solution              | (1.75)                                                         | (0.25)         | (2)            | (2)             | (3)          |                        |           |
| Oxalate               | 19.20<br>(1.71)                                                | 2.54<br>(0.23) | 4.20<br>(1.97) | 9.19<br>(1.97)  | 10.15<br>(3) |                        |           |
| Oxide                 | 36.14<br>(1.69)                                                | 4.65<br>(0.22) | 7.91<br>(1.93) | 17.85<br>(1.99) | 19.51<br>(3) | 850                    | 160       |
| Solution              | (1.7)                                                          | (0.3)          | (2)            | (2)             | (3)          |                        |           |
| Oxalate               | 19.48<br>(1.62)                                                | 3.08<br>(0.26) | 4.50<br>(1.94) | 9.50<br>(1.89)  | 10.89<br>(3) |                        |           |
| Oxide                 | 34.91<br>(1.65)                                                | 5.85<br>(0.28) | 8.03<br>(1.98) | 17.03<br>(1.92) | 19.30<br>(3) | 845                    | 90        |
| Solution              | (1.6)                                                          | (0.4)          | (2)            | (2)             | (3)          |                        |           |
| Oxalate               | 18.16<br>(1.57)                                                | 4.08<br>(0.36) | 4.55<br>(2.05) | 9.84<br>(2.03)  | 10.55<br>(3) |                        |           |
| Oxide                 | 37.00<br>(1.62)                                                | 8.27<br>(0.37) | 8.60<br>(1.95) | 18.53<br>(1.92) | 20.70<br>(3) | 810                    | 45        |

<sup>a</sup> The molar ratios of the cations in the oxalates and the oxides are based on three for  $\text{Cu}^{2+}$ .

<sup>b</sup> Molar ratios of the cations in the starting solution.

The sublimation of  $\text{PbO}$ —found to begin at  $1000^\circ\text{C}$  for  $\text{Pb}(\text{C}_2\text{O}_4)$ —did not start at temperatures below  $1100^\circ\text{C}$ .  $\text{Bi}_2\text{O}_3$ , which sublimed at  $1150^\circ\text{C}$  in the oxalate, remained in the solid phase until  $1300^\circ\text{C}$  in the mixed oxidic compounds.

### 2.5. Formation and Characterization of Superconducting Oxides

The conversion of the coprecipitated oxalates to superconducting Pb-doped Bi-Sr-Ca-Cu oxides was carried out in a standard furnace in air at various temperatures between  $810$  and  $850^\circ\text{C}$  ranging from 45 to 160 hr. The heating and cooling rates were 1 K

$\text{min}^{-1}$  in all experiments. The calcined powders were then compressed at room temperature into disks of 13 mm diameter at a pressure of 7000 bar and sintered at the same temperature as before for 8 hr in air.

The superconducting oxides calcined under various conditions were analyzed by AAS. The AAS analysis of the oxides prepared by different heat treatments did not reveal any changes in the molar ratios of the cations with respect to the oxalate precursors. No loss of lead was observed for firing temperatures up to  $850^\circ\text{C}$ . The average valency of copper as analyzed by the titration method described above was found

to be  $2.20 \pm 0.01$  with the pure phase material and  $2.18 \pm 0.01$  for samples consisting of both 2223- and 2212-phase material.

The characterization of the superconducting ceramics fabricated was mainly performed by X-ray diffraction and by temperature-dependent resistance measurements. These investigations revealed that almost single-phase high  $T_c$  material can be obtained after proper heat treatment for  $\text{Pb}^{2+}$  concentrations of  $0.2 \leq y \leq 0.4$ . Molar ratios of  $\text{Pb}^{2+}$  greater than 0.4 were not investigated in this study. With  $y < 0.2$  the material consisted of either the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  phase (2212 phase) (measured  $T_c(0) \sim 77$  K) together with  $\text{Ca}_2\text{CuO}_3$  and  $\text{CuO}$  or of a mixture of these phases and the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  phase (2223 phase). Almost single-phase high  $T_c$  material was obtained after heat treatment at temperatures between 810 and 850°C for about 90–100 hr in air and  $y > 0.2$ . Shorter but also longer heat treatments yielded predominantly the 2212 phase  $\text{Ca}_2\text{CuO}_3$  and  $\text{CuO}$ . The best results have been achieved with samples calcined at 810°C for 100 hr. The X-ray diffraction patterns of such a sample shown in Fig. 4 indicates a rather pure high  $T_c$  2223 phase that is characterized by the (002) re-

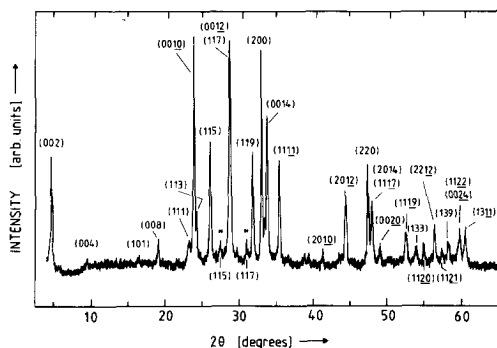


FIG. 4. X-ray diffraction pattern of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  superconductor produced from the corresponding coprecipitated oxalate. Calcination at 810°C for 100 hr. \* Indicates peaks due to small amounts of the 2212 phase.

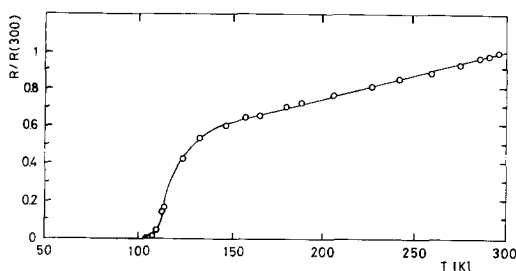


FIG. 5. Temperature dependence of the electrical resistance of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . The sample was the same as that used for the X-ray diffraction pattern presented in Fig. 4.

flection at  $2\theta = 4.7^\circ$  ( $\text{CuK}\alpha$ ). Using tetragonal structure with  $a = 0.541$  nm and  $c = 3.710$  nm, we were able to index nearly all of the X-ray diffraction spectrum as shown in Fig. 4. Very small amounts of the 2212 phase were also found in this sample and are indicated by asterisks.

Scanning electron microscopy on the 2223 phase showed platelike crystals with a thickness of less than 1  $\mu\text{m}$  and a grain size around 3  $\mu\text{m}$ . The temperature dependence of the normalized resistance of such a sample with  $y = 0.4$  is shown in Fig. 5. Metallic behavior is observed from room temperature to 125 K. Zero resistance was obtained, typically, at a temperature of about 106 K.

### 3. Conclusion

Coprecipitation of  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  as oxalates from aqueous acetic acid solutions yields suitable precursor material to fabricate almost single-phase Pb-doped Bi–Sr–Ca–Cu–O superconducting ceramics with zero-resistance temperatures of, typically, 106 K. The homogeneous distribution of cations in the oxalate precursor permitted calcination temperatures as low as 810°C. No loss of lead upon conversion of the coprecipitated oxalate into the superconducting oxide was found for firing temperatures up to 850°C.

## Acknowledgment

The authors thank Mr. K. Kellner for his assistance in the thermogravimetry and X-ray diffraction measurements and Dr. K. Lübke for the electron microscopy. Two of us (X. Z. W. and D. B.) thank the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich for financial support.

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