JOURNAL OF SOLID STATE CHEMISTRY **86**, 293–299 (1990)

Formation of Superconducting $Bi_{2-y}Pb_ySr_2Ca_2Cu_3O_x$ from Coprecipitated Oxalates

KLAUS BERNHARD AND GERHARD GRITZNER*

Institut für Chemische Technologie Anorganischer Stoffe, Johannes Kepler Universität Linz, A-4040 Linz, Austria

XIAN-ZHONG WANG AND DIETER BÄUERLE*

Institut für Angewandte Physik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

Received February 9, 1990

The conditions for the coprecipitation of Bi^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, and Cu^{2+} as oxalates are reported. These oxalates were used as precursors for the formation of $Bi_{2-y}Pb_ySr_2Ca_2Cu_3O_x$ 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.

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 $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ (δ 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 $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ 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 Bi^{3+} by 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 PbO, Bi_2O_3, CuO, $SrCO_3$, and $CaCO_3$ (*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 NaOH. This

---

* To whom correspondence should be addressed.

0022-4596/90 $3.00

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 $BiSrCaCu_2O_{6-z}$ and $Bi_2Sr_2CaCu_2O_{8+z}$.

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 $Bi_{2-y}Pb_ySr_2Ca_2Cu_3O_x$ 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 Cu$K\alpha$ 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 Bi^{3+}, Sr^{2+}, Ca^{2+}, and 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 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 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 dm^{-3} $FeSO_4$, 1.5 mole dm^{-3} sulfuric, and 1.5 mole dm^{-3} hydrochloric acid. Upon dissolution of the compound the unreacted Fe^{2+} was titrated with a 0.02 mole dm^{-3} $K_2Cr_2O_7$ 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 $Bi_{2-y}Pb_ySr_2Ca_2Cu_3O_x$ (y: 0 to 0.4) material were precipitated as oxalates in the following manner: $SrCO_3$ (Merck, extra pure), Bi_2O_3 (Merck, extra pure), $CaCO_3$ (Merck, volumetric standard), $Cu(CH_3COO)_2 \cdot H_2O$ (Merck, >99%), and $Pb(CH_3COO)_2 \cdot 3\,H_2O$ (Merck, >99.5%) were dissolved in such quantities in 25 vol% acetic acid that the solution contained 0.02 mole dm^{-3} Ca^{2+} and Sr^{2+} as well as 0.03 mole dm^{-3} Cu^{2+}. Depending on the desired final composition of the superconducting material the concentration of Bi^{3+} varied between 0.016 and 0.02 mole dm^{-3} and the concentration of Pb^{2+} from 0.004 mole dm^{-3} to zero. Clear, blue solutions were obtained in all cases. In a typical experiment 65 ml of a 0.8 mole dm^{-3} aqueous solution of oxalic acid (Merck, >99.5%) was added dropwise under stirring into 500 ml of the solution containing 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°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 Bi^{3+}, less than 0.5% of Pb^{2+}, less than 1.9% of Sr^{2+}, less than 1.5% of Ca^{2+}, and less than 1.0% of Cu^{2+} remained in solution.

This procedure was also employed to prepare the following individual oxalates: $Pb(C_2O_4)$, $Ca(C_2O_4) \cdot H_2O$, $Sr(C_2O_4) \cdot H_2O$, and $Cu(C_2O_4) \cdot 2.5\ H_2O$. The precipitation of Bi^{3+} as oxalate under the above conditions yielded a compound, which based on our analysis can best be described as Bi $(OH)_{0.5}(C_2O_4)_{1.25}$.

In order to obtain a more detailed picture of the coprecipitation process, oxalic acid was added stepwise to a solution containing 0.016 mole dm^{-3} Bi^{3+}, 0.004 mole dm^{-3} Pb^{2+}, 0.02 mole dm^{-3} Sr^{2+}, 0.02 mole dm^{-3} Ca^{2+}, and 0.03 mole dm^{-3} 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 $(C_2O_4)^{2-}$ 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 Cu^{2+} and Pb^{2+} precipitate before the Bi^{3+}, Sr^{2+}, and Ca^{2+}.

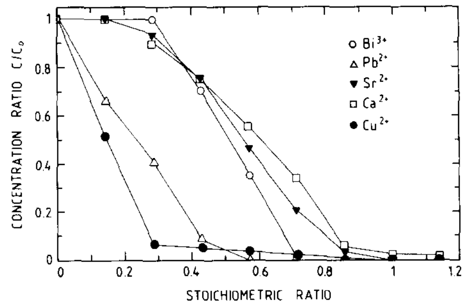

FIG. 1. Concentration of Cu^{2+}, Pb^{2+}, Bi^{3+}, Ca^{2+}, and Sr^{2+} in solution relative to the respective concentration in the starting solution as a function of the amount of oxalic acid added. Original concentrations in solution: Bi^{3+}, 0.016 mole dm^{-3}; Pb^{2+}, 0.004 mole dm^{-3}; Sr^{2+},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

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 $Cu(C_2O_4) \cdot 2.5\ H_2O$ (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 Ca^{2+}, Sr^{2+}, or Bi^{3+} (Fig. 2b). Surprisingly, despite the quite different precipitation behavior of Cu^{2+} and Pb^{2+} on the one hand and of Bi^{3+}, Sr^{2+}, and 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 $Cu(C_2O_4) \cdot 2.5\ H_2O$, nor with those of any of the other individual oxalates of Bi^{3+}, Pb^{2+}, Ca^{2+}, or 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

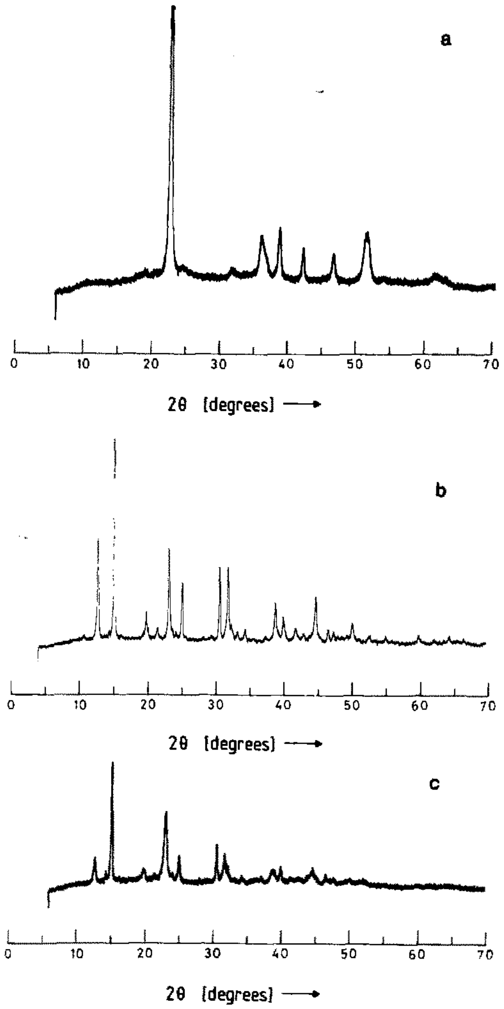

FIG. 2. X-ray diffraction patterns of some of the oxalates synthesized. (a) $Cu(C_2O_4) \cdot 2.5\ H_2O$; (b) Bi^{3+}-, Sr^{2+}-, and Ca^{2+}-coprecipitated oxalate; (c) Bi^{3+}-, Pb^{2+}-, Sr^{2+}-, Ca^{2+}-, and Cu^{2+}-coprecipitated oxalate.

scanning electron microscopy, was found to be below 1 μm.

2.4. Thermogravimetry

The thermogravimetric measurements on coprecipitated and individual oxalates were performed under argon atmosphere and at a heating rate of 5 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°C originate from the loss of water. The rather dramatic weight loss at around 300°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°C is similar to that observed for the individual oxalates. For temperatures above 600°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°C is due to the loss of CO_2 from $CaCO_3$ and $SrCO_3$. 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°C for $CaCO_3$ and between 900 and 1100°C for $SrCO_3$.

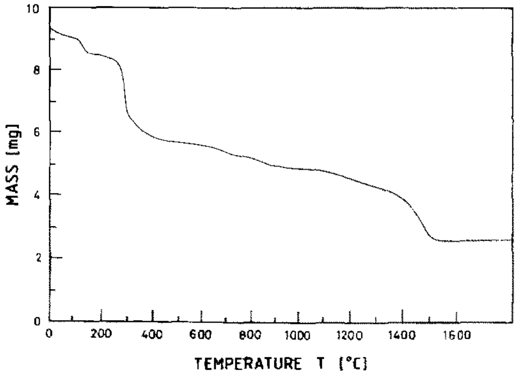

FIG. 3. Thermogravimetry curve of coprecipitated Bi^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, Cu^{2+} oxalate.

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

[a] The molar ratios of the cations in the oxalates and the oxides are based on three for Cu^{2+}.

[b] Molar ratios of the cations in the starting solution.

The sublimation of PbO—found to begin at 1000°C for $Pb(C_2O_4)$—did not start at temperatures below 1100°C. Bi_2O_3, which sublimed at 1150°C in the oxalate, remained in the solid phase until 1300°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°C ranging from 45 to 160 hr. The heating and cooling rates were 1 K 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°C. The average valency of copper as analyzed by the titration method described above was found to be 2.20 ± 0.01 with the pure phase material and 2.18 ± 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 Pb^{2+} concentrations of $0.2 \leq y \leq 0.4$. Molar ratios of Pb^{2+} greater than 0.4 were not investigated in this study. With $y < 0.2$ the material consisted of either the $Bi_2Sr_2Ca Cu_2O_{8+\delta}$ phase (2212 phase) (measured $T_c(0) \sim 77$ K) together with Ca_2CuO_3 and CuO or of a mixture of these phases and the $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ 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 Ca_2CuO_3 and 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) reflection at $2\Theta = 4.7°$ (Cu$K\alpha$). 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.

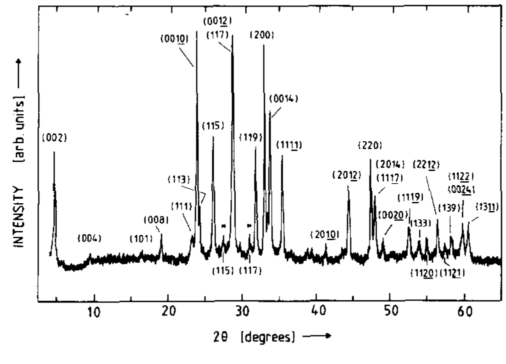

FIG. 4. X-ray diffraction pattern of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2 Cu_3O_x$ superconductor produced from the corresponding coprecipitated oxalate. Calcination at 810°C for 100 hr. * Indicates peaks due to small amounts of the 2212 phase.

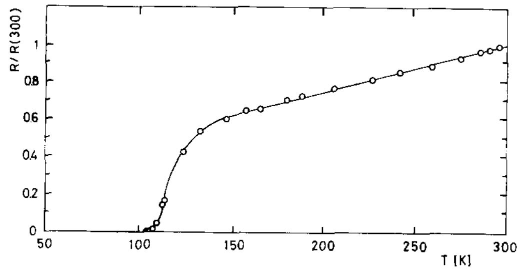

FIG. 5. Temperature dependence of the electrical resistance of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$. The sample was the same as that used for the X-ray diffraction pattern presented in Fig. 4.

Scanning electron microscopy on the 2223 phase showed platelike crystals with a thickness of less than 1 μm and a grain size around 3 μm. 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 Bi^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, 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.

References

1. H. Maeda, Y. Tanaka, M. Fukutumi, and T. Asano, *Japan. J. Appl. Phys.* **27**, L209 (1988).
2. R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, *Phys. Rev. Lett.* **60**, 1174 (1988).
3. C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, *Z. Phys. B* **68**, 421 (1987).
4. J. M. Tarascon, W. R. McKinnon, P. Barbox, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. Lepage, N. Stoffel, and M. Giroud, *Phys. Rev. B* **38**, 8885 (1988).
5. A. Ono, *Japan. J. Appl. Phys.* **27**, L1213 (1988).
6. M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii, and H. Mazaki, *Japan. J. Appl. Phys.* **27**, L1041 (1988).
7. B. W. Statt, Z. Wang, M. J. G. Lee, J. V. Yakhmi, P. C. Decamargo, J. F. Major, and J. W. Rutter, *Physica C* **156**, 251 (1988).
8. Y. Zhang, Z. Fang, M. Muhammed, K. V. Rao, V. Skumryev, H. Medelius, and J. L. Costa, *Physica C* **157**, 108 (1989).
9. V. Slusanenko, K. R. Thampi, and J. Kiwi, *J. Solid State Chem.* **79**, 277 (1989).
10. G. Jander, K. F. Jahr, and H. Knoll, "Maßanalyse," p. 74, Walter de Gruyter, Berlin (1973).