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Preparation and Characterization of Superconducting $(Bi,Pb)_2Sr_2Ca_2Cu_3$ Oxides with T_c above 110 K by Coprecipitation in Triethylamine Media

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Bi(Pb)–Sr–Ca–Cu–O superconducting powders were prepared from an aqueous solution containing Bi, Pb, Sr, Ca, and Cu salts and oxalic acid via coprecipitation using triethylamine as a base. The dried precipitate was found to have satisfactory stoichiometry and a particle size of 0.3 μm. Subsequent calcination at 800 °C for 12 h and sintering at 860 °C for 72 h yield superconducting with T_c above 110 K. This process can be employed in a large-scale preparation of the Bi(Pb)–Sr–Ca–Cu–O superconducting powder.

Introduction

The Bi–Sr–Ca–Cu–O (BSCCO) superconductor was first discovered by Maeda[3] et al. with two superconducting phases; the low-T_c phase (T_c = 80 K) belongs to $Bi_2Sr_2CaCu_2O_y$ (2212) and the high-T_c phase (T_c = 110 K) is derived from $Bi_2Sr_2Ca_2Cu_3O_y$ (2223). However, it is rather difficult to prepare the high-T_c phase alone. Recently, Tanaka[2] et al. have succeeded in doping Pb into the BSCCO superconducting materials and thus enhanced the ratio of the 110 K (2223) phase. The conventional method for the preparation of this compound by means of a solid-state reaction has many inherent problems, e.g., poor homogeneity, large particle size, lack of reproducibility, and long heat-treatment times. Coprecipitation may be a better process because it can produce powders with smaller particle sizes and higher homogeneity. Two common coprecipitation methods were employed. The first uses oxalic acid as precipitant, adjusting the pH with NaOH[5] or KOH;[6] the other uses ammonium oxalate directly as precipitant. However, the former has drawbacks such as contamination of the product with Na^+ or K^+ ions, while the latter exhibits nonstoichiometry because of the easy complexation of the ammonia molecule with the copper(II) ion. In this paper, we demonstrate a new aqueous coprecipitation process using oxalic acid as a precipitant with triethylamine for pH adjustment in the preparation of Bi(Pb)–Sr–Ca–Cu–O superconducting powders of high homogeneity and stoichiometry.

Experimental Procedures

All chemicals were high-purity grade purchased from Merck AG without further treatment. Deionized water was used for all chemical procedures.

The $Bi(NO_3)_3{\cdot}5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2{\cdot}2H_2O$, and $Cu(NO_3)_2{\cdot}3H_2O$ were weighed in the molar ratio 1.4/0.6/2/2/3 (using 0.005 mol of Bi^{3+}) and dissolved in 10 mL of 2 M nitric acid with constant stirring. The aqueous $Et_3N/H_2C_2O_4$ solution was prepared with a 20% excess of oxalic acid (as required for the precipitation of the total metal ions) dissolved in 50 mL of H_2O with Et_3N added to adjust the $Et_3N/H_2C_2O_4$ ratio from 1 to 3. The mixture was vigorously stirred for 10 min to ensure complete dissolution. The solution of the metal nitrate salts was added dropwise to the $Et_3N/H_2C_2O_4$ solution with vigorous stirring. During the mixing, a pale blue powder gradually formed. The solution was cooled with an ice–water bath while being stirred. After 0.5 h the mixture was filtered, and the precipitate was dried at 140 °C for 6 h. The dehydrated powders were calcined at 800 °C in air for 10 h and then pressed into cylindrical pellets of 2-mm thickness and 10-mm diameter with a pressure of 2 $tons{\cdot}cm^{-2}$. The finally sintering was done at 860 °C in air for 12–72 h. A recent experiment indicates that calcining at 845 °C for only 24–28 h can also give a similar product.

The amount of metal residue in the filtrate was analyzed by using a Plasmakon S35 inductively coupled plasma–atomic emission spectrometer (ICP–AES). The particle size of the precipitate was measured with a Coulter Model N4 particle analyzer. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of dried powders were performed by a TGD 7000 instrument (Ulvac Co.). The ac electric resistance measurements were made by using a standard four-probe technique. Fine copper wire, which served as the voltage and current leads, was attached to the sample with air-drying silver paste. A Linear Research Inc. LR-400 personal computer interface, which is capable of fully automated data acquisition, was employed in the resistance measurements. Magnetization data were recorded with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in which the sample was moved slowly through the pick-up coil. The structure of the sintered powder was determined on a Philips PW-1700 X-ray diffractometer (XRD) using Cu Kα radiation.

Results and Discussion

1. The $Et_3N/H_2C_2O_4$ Mixture as a Precipitant. Usually the adjustment of the pH is a crucial factor in the quantitative precipitation of metal ions from an aqueous solution. In order to circumvent possible contamination from nonvolatile metal ions such as K^+ and Na^+ introduced from KOH or NaOH, a base such as ammonia or an organic amine is commonly employed. In the present study a mixture of triethylamine and oxalic acid was used. Triethylamine (being a liquid with reasonably high solubility in water) can be easily handled, and because of its low volatility, its concentration can be kept virtually constant during the chemical processing. Furthermore, triethylamine has a higher basicity and less complexing ability toward the Cu(II) ion as compared with ammonia, which renders it easier to control the solution at higher pH. A lower dielectric constant, as compared with those of ammonia and water, is also helpful for the quantitative precipitation of the metal ions.

2. The Composition and Thermograms of the Precipitates. As the nitrate solution was added to $Et_3N/H_2C_2O_4$ solutions with varying ratios between 1 to 3, the pH increased gradually up to the ratio of 2 and then increased abruptly for ratios larger than 2.2, as shown in Figure 1. The color of the filtrates was observed to change from colorless to pale blue and finally to deep blue, indicating the dissolution of the Cu(II) ion from the precipitate into the solution at higher pH. The elemental analyses on the filtrates using an ICP–AES, as shown in Figure 2, indicate that all the metal ions can be stoichiometrically precipitated within the $Et_3N/H_2C_2O_4$ ratios between 1.8 to 2.2. At higher ratios considerable losses of Bi^{3+} and Cu^{2+} ions into the solution were observed. A dried pale blue precipitate with a particle size of 0.3 μm was obtained under optimum conditions.

The DTA/TGA thermograms (Figure 3) show a gradual weight loss from 100 to 220 °C. A sharp weight loss accompanied by two exothermic peaks between 220 and 350 °C was observed, which is indicative of the loss of organic moieties. When the sample was heated to 800 °C, the weight loss was due to the

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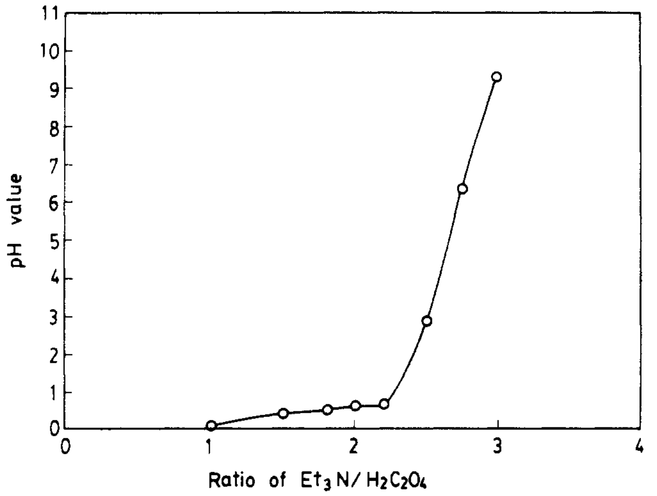

Figure 1. Dependence of the $Et_3N/H_2C_2O_4$ ratio on the final pH of the solution.

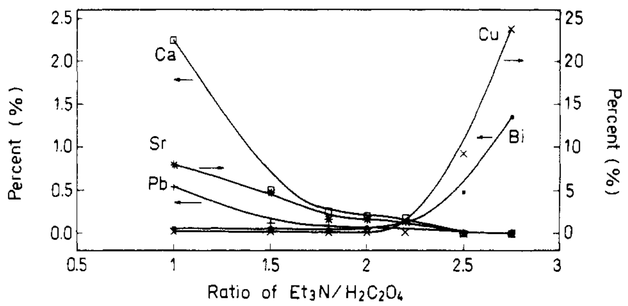

Figure 2. Dependence of the $Et_3N/H_2C_2O_4$ ratio on the metal ion residuals in the filtrate.

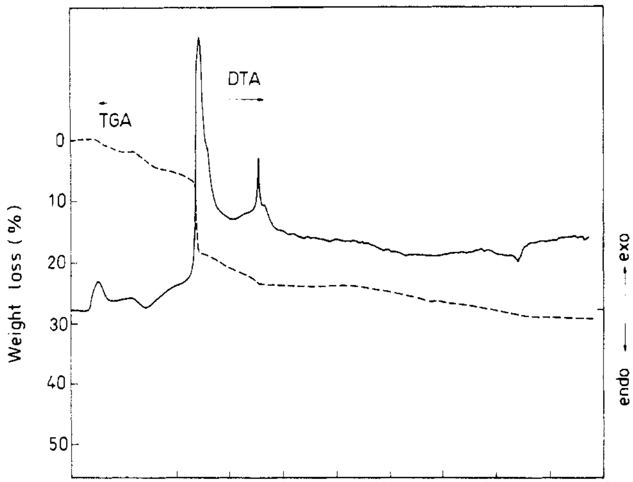

Figure 3. TGA/DTA thermograms for the precipitate.

Table I. Characteristics of the Superconducting Specimens Prepared under Various Conditions

no.	$Et_3N/H_2C_2O_4$	temp, °C	time, h	T_0, K
C1	1.5	850	12	72
C2	1.5	860	12	83
C3	1.5	860	72	108
C4	1.8	860	72	110
C5	2.0	850	12	67
C6	2.0	860	12	72
C7	2.0	860	72	106
C8	2.2	860	72	105
C9	2.5	850	12	63
C10	2.5	860	12	65
C11	2.5	860	72	63
C12	3.0	860	72	semiconductor

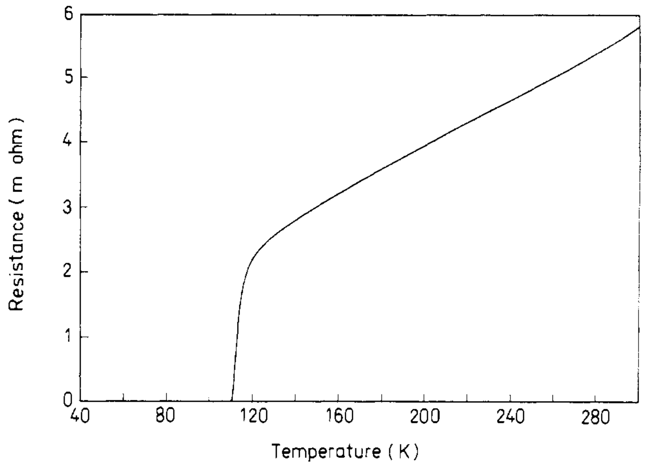

Figure 4. Temperature dependence of the resistance for sample C4.

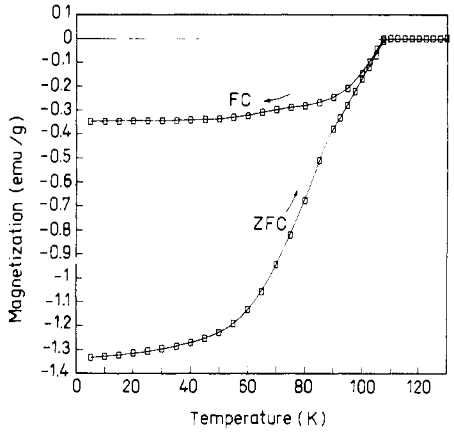

Figure 5. Temperature dependence of magnetization for sample C4.

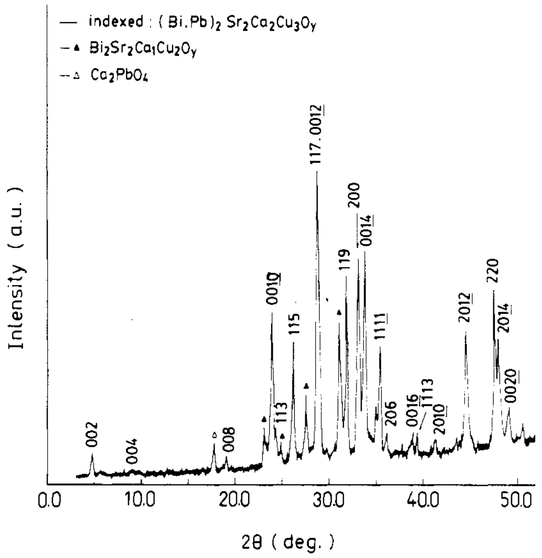

Figure 6. XRD pattern for sample C4.

decomposition of $SrCO_3$ and $CaCO_3$ into SrO and CaO. Above 800 °C, Bi(Pb)-Sr-Ca-Cu-O compounds will form.

3. Superconducting Characteristics. Table I summarizes the zero-resistance tempertures (T_0) of the superconducting powders prepared under various conditions. A powder with T_0 between 105 to 110 K could be produced when the $Et_3N/H_2C_2O_4$ ratios were adjusted between 1.5 to 2.2 and sintered at 850 °C for 72 h.

Figure 4 shows the temperature dependence of the resistance curve for the C4 specimen. Properties of the superconducting temperature for C4 are T_{onset} = 128 K, T_c = 114 K, T_0 = 110 K, and ΔT = 7 K.

Figure 5 displays the temperature dependence of the field-cooled (Meissner effect) and zero-field-cooled (shielding effect) magnetization for C4 measured in a field of 100 Oe between 5 and 130 K with a SQUID magnetometer. As shown in Figure 5, a superconducting transition at T_0 = 110 K is observed, which is consistent with the resistance measurement. A small amount of 80 K phase is seen coexisting with the 110 K phase. The estimated Meissner fraction is about 30%.

Figure 6 shows the XRD pattern for C4. The major peaks belong to $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (T_c = 110 K) with a small amount of $(Bi,Pb)_2Sr_2CaCu$ (T_c = 80 K) and an impurity phase of Ca_2PbO_4.[8,9]

Conclusion

A high-T_c superconducting oxide powder of Bi(Pb)–Sr–Ca–Cu–O has been prepared by means of coprecipitation using Bi, Pb, Sr, Ca, and Cu nitrates as starting materials with oxalic acid/triethylamine as a precipitant. Fine, homogeneous stoichiometric powders were obtained by using optimum $Et_3N/H_2C_2O_4$ ratios between 1.5 to 2.2. Subsequent calcination at 800 °C for 10 h and sintering at 860 °C for 72 h are recommended for the 110 K Bi-base superconductor. All the experimental conditions can be easily controlled and reproduced. This technique has great potential for a scale-up production.

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Registry No. $Bi(NO_3)_3$, 10361-44-1; $Pb(NO_3)_2$, 10099-74-8; $Sr(NO_3)_2$, 10042-76-9; $Ca(NO_3)_2$, 10124-37-5; $Cu(NO_3)_2$, 3251-23-8; Et_3N, 121-44-8; $H_2C_2O_4$, 144-62-7; $(Bi,Pb)_2Sr_2Ca_2Cu_3O_4$, 116739-98-1.

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A Bromide Analogue of a One-Dimensional Ising Ferromagnet: Trimethylammonium *catena*-Bis(μ-bromo)diaquoiron(II) Bromide

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The crystal structure of the title compound, FeTAB, has been determined by X-ray diffraction and has been found to be isomorphous to that of the chloride analogue, FeTAC. The structure consists of chains of bibromide-bridged Fe^{2+} ions extending along the *b* axis of the orthorhombic unit cell (space group *Pnma*, a = 17.287 (3) Å, b = 7.651 (2) Å, c = 8.320 (3) Å, $R(F_o)$ = 0:0494, $R_w(F_o)$ = 0.0488). The chains are linked into a 2-dimensional network in the *c* direction by hydrogen bonding to a third bromide ion; the resulting planes are well isolated in the *a* direction by the organic molecules. The low-temperature magnetic susceptibility of polycrystalline samples can be modeled by using a one-dimensional ferromagnetic Ising model with a molecular field correction. The exchange parameters are estimated to be J/k = 4 K and $z'J'/k$ = −0.2 K, indicating that FeTAB has an intrachain exchange constant only one-fourth of that found in the chloride analogue while the interchain interactions are more than 10-times greater. Antiferromagnetic ordering is observed in the Mössbauer spectra near 1.3 K. Analysis of the polycrystalline spectra shows that the internal magnetic field (and easy axis of magnetization) for FeTAB lies close to the *ab* plane, as previously found for FeTAC.

Introduction

The series of isostructural 3d M(II) linear-chain compounds $[(CH_3)_3NH]MCl_3{\cdot}2H_2O$ (abbreviated as MTAC), for M = Mn, Fe, Co, Ni, and Cu, has been thoroughly studied.[1-11] All of the compounds consist of dichloro-bridged chains of M^{2+} ions, held together into layers by hydrogen bonding to a noncoordinated chloride ion. The resulting layers are well separated by the bulk of the trimethylammonium ions. Magnetic studies have shown the magnetic interactions to reflect the structural anisotropy, these compounds possessing a pronounced one-dimensional character. The interactions between adjacent chains are normally only a few percent of that of the intrachain exchange, although in FeTAC the magnetic isolation has recently been shown[5] to be a factor of 10 better. The low-dimensional character causes the magnetic ordering temperatures to occur in the liquid-helium temperature region.

The ability of this structure to include all of the 3d metal ions from manganese to copper presents a valuable framework in which to study both the effects of the number of 3d electrons in the magnetic ion upon magnetic behavior and to study the magnetic behavior of mixed-metal systems. Examination of the pure compounds has shown that the dominant, intrachain interactions are ferromagnetic for all the members of the MTAC family, with the exception of MnTAC. The manganese[2-4] and nickel[8,9] compounds have been found to behave as essentially Heisenberg linear chains, although single-ion effects are not negligible. The cobalt[6,7] and ferrous[5] compounds are Ising systems, with spin canting present in CoTAC, which causes it to order as a weak ferromagnet. The copper compound was the first reported example of a ferromagnetic $S = {}^1/_2$ Heisenberg linear chain.[10] There is, however, a significant amount of both Ising component in the exchange interaction and interchain exchange present in this compound, which lead to both spin dimensionality and lattice dimensionality crossovers at low temperature.[11]

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